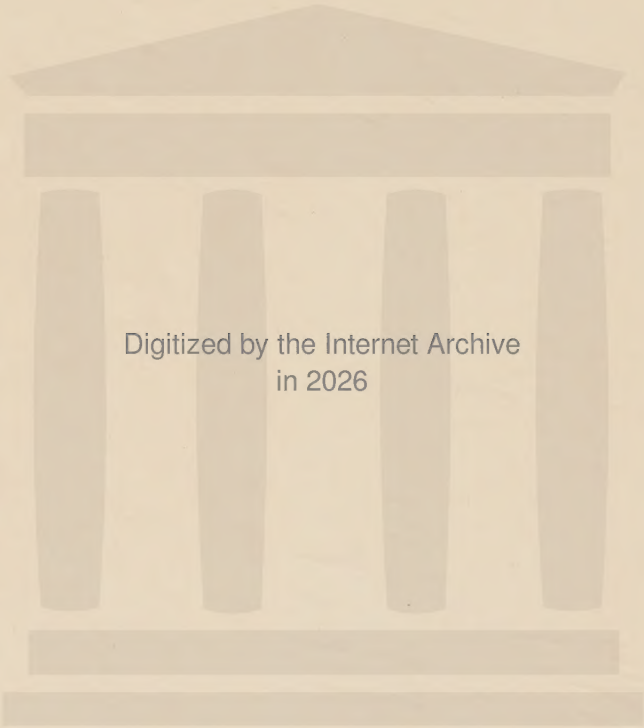
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TECHNICAL
METHODS OF ANALYSIS

TECHNICAL METHODS OF ANALYSIS

As Employed in the Laboratories of Arthur D. Little, Inc., Cambridge, Mass.

Edited by

ROGER CASTLE GRIFFIN, A.M., S.M.
Director of Analytical Department

Second Edition

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THIS BOOK IS AFFECTIONATELY

DEDICATED TO THE MEMORY OF MY FATHER

Roger Burrill Griffin

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PREFACE

This book contains a representative selection of analytical methods which have been adopted as standard procedures in a large commercial laboratory engaged in technical analysis. With very few exceptions the methods here given have been used many times in this laboratory and have been proved to give satisfactory results in the hands of different analysts. In certain cases it has been thought best to include, for the sake of completeness, certain standard procedures which have not been thoroughly tested in our laboratory but which have, nevertheless, received official recognition from an authoritative body of chemists. Such a case is the method for Fusel Oil in Grain Alcohol on page 99.

Endeavor has been made to give such directions in each procedure that any one reasonably familiar with analytical technique can readily follow them. A certain amount of cross referencing has been necessary on account of economy of space but, in order to avoid the annoyance caused by carrying this to extremes, the directions, when they are not too long, have been repeated in most cases.

No attempt has been made to give experimental data to show the accuracy of the method nor in most cases to enter into the theory of the procedure. On the other hand in many cases it has seemed advisable to give brief descriptions of the properties which a given material should normally possess and sufficient other information to enable the analyst to translate his results into practical language. Certain specifications and requirements of an authoritative nature have also been included.

It is obviously impossible in a book of this size to enter all the fields of analytical chemistry. Certain classes of work, such as drugs, alkaloids, and medicines, have been omitted, as they are of interest mainly to specialists in these lines. This is also true of the rare elements and, to a certain extent, of gas analysis. The analysis of mineral rocks, glasses, and vitreous materials

would require a book in itself. The present book is not intended for the specialist, confining himself to comparatively narrow limits. It aims rather to include methods which are typical of the procedures employed in the usual commercial analyses. Certain special methods have been included, when not too long, in the belief that they are not otherwise readily obtainable and that they illustrate procedures which may be applicable to other problems. The analyst whose particular problem is not covered by the methods here given is referred to the bibliography on page 887.

Some of the methods herein described are original. By far the greater number, however, have been obtained from other sources. In many cases they have been adopted without change; others have been modified in the light of experience gained from their use. Since the collection of methods has been built up gradually over a period of years, it is not possible in every case to give proper credit for the original source. The methods of the Association of Official Agricultural Chemists have been found particularly valuable, although it has sometimes seemed more convenient to change their arrangement. The various publications of the United States Bureaus at Washington have also been drawn upon freely.

In presenting the second edition, the methods of the previous edition have been thoroughly revised to bring them up to date. Not only have many of the methods appearing in the first edition been expanded and augmented but some 40 additional methods have been included. The chapter on Foods in particular has been considerably elaborated and an entire new chapter has been included on Water, Sewage and Soils.

The analytical tables have been confined strictly to those concerned with quantitative chemical analysis. The values in these tables have all been independently recalculated from the 1925 International Atomic Weights. Every effort has been made to have them correct. If any errors should be discovered the editor will be grateful to those who bring them to his attention. References to other tables are given in the text; and tables of properties, specific gravity tables, etc., may be found in the handbooks referred to in the bibliography. This bibliography aims to include at least one authoritative book in each of the fields of analytical chemistry.

Numerous cuts have been included as aids to the description of procedures. Acknowledgment is made for certain of these as follows: Fig. 10, American Society for Testing Materials, Standard D 21–16; Fig. 12, U. S. Bur. Mines *Tech. Paper* 166, Petroleum Technology 39; Figs. 22, 23, 25, 26 and 27, *Paper* **25**, No. 15, 19–23 (1919); Figs. 28, 29 and 30, Bureau of Chem., *Circular* 107; Figs. 42 and 43, Am. Soc. Test. Mat., Standard C 9–17; Fig. 44, courtesy of the Fairbanks Co. The table of constants of oils, fats and waxes on pages 300–307 was prepared from data obtained largely from Lewkowitsch: "Chemical Technology and Analysis of Oils, Fats and Waxes."

In the preparation of the first edition the editor wishes to express his appreciation to Dr. H. P. Talbot for valuable criticisms and suggestions and to Dr. R. S. Williams for reading part of the manuscript. Thanks are also especially due to Dr. C. J. West, who prepared the bibliography and whose aid in arranging the manuscript and reading the proof is greatly appreciated. Mr. H. C. Parish and Mrs. Helen B. Colson also rendered valued assistance in checking the numerical tables.

The preparation of the second edition was only undertaken as the result of considerable pressure and numerous requests. It was necessary to do practically all of the work evenings and it is doubtful if it would have been accomplished without the enthusiastic encouragement and willing assistance of my wife.

ROGER C. GRIFFIN.

NEEDHAM, MASS.
March, 1927

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TECHNICAL METHODS OF ANALYSIS

CHAPTER 1

REAGENTS

LIQUID REAGENTS

General.—In making up reagents always use chemicals of highest purity, unless otherwise instructed. In the following directions water is understood to be distilled water. All solutions should be filtered unless perfectly clear or unless directions state to the contrary. Formulas here given are generally for 1 liter of reagent. The ordinary green glass acid bottle contains about 2.5 liters.

Acetic Acid, Glacial.—Contains 99.5% $HC_2H_3O_2$. The sp. gr. is about 1.058.

Acetic Acid, Dilute (sp. gr. 1.044).—Mix 400 cc. of glacial acetic acid with 1 liter of water. This solution contains about 30% of $HC_2H_3O_2$.

Alcoholic Potash (Half-normal).—Dissolve 30 grams of pure KOH (preferably purified by alcohol) in 1 liter of 95% alcohol.

NOTE.—The alcohol before use should be tested with a little NaOH and if it gives a decidedly yellow solution, showing an excessive aldehyde content, treat it as follows: Dissolve about 1.5 grams of $AgNO_3$ in 3 cc. of water and add to 1 liter of the alcohol. Shake thoroughly. Dissolve 3 grams of NaOH in 15 cc. of warm alcohol, cool and add to the main solution. Shake thoroughly, let settle, siphon off the clear liquid and distill, adding a few pieces of pumice to prevent bumping.

The alcohol and KOH mixture should be allowed to stand until all the KOH has dissolved and then filtered rapidly, or siphoned off, to remove the insoluble carbonate.

Alumina Cream.—Prepare a cold saturated solution of alum (KAl sulfate) in water. Add NH_4OH with constant stirring

until the solution is alkaline to litmus; let settle and wash by decantation with water until the wash water gives only a slight test for sulfate with $BaCl_2$. Pour off the excess of water and store the residual cream in a stoppered bottle.

Ammonium Acetate.—To 1250 cc. of glacial acetic acid add cautiously 1000 cc. of conc. NH_4OH (sp gr. 0.90), a little at a time, with constant stirring, and cooling if necessary. The solution contains about 70% of ammonium acetate, $NH_4C_2H_3O_2$.

Ammonium Carbonate.—Dissolve 250 grams of ammonium carbonate crystals in 1 liter of water and add 100 cc. of conc. NH_4OH. This solution contains about 22% of the carbonate, which is generally assigned the formula $(NH_4)_2CO_3 \cdot NH_4CO_2NH_2$.

Ammonium Chloride (10%).—Dissolve 100 grams of NH_4Cl in water in a liter volumetric flask and dilute to the mark.

Ammonium Hydroxide, Conc. (sp. gr. 0.90).—The solution contains 28–29% of NH_3 by weight.

Ammonium Hydroxide, Dilute (sp. gr. 0.96).—Mix 400 cc. of conc. NH_4OH with 700 cc. of water. The solution contains about 10% of NH_3 by weight.

Ammonium Molybdate. Solution No. 1.—Weigh 113 grams of 100% C. P. molybdic acid (MoO_3) or an equivalent amount of weaker acid. Add 300 cc. of water, 175 cc. of conc. NH_4OH, and, after mixing, add *slowly* with stirring 75 cc. of conc. HNO_3.

Solution No. 2.—To 1200 cc. of water add 500 cc. of conc. HNO_3.

When both solutions are perfectly cold, pour No. 1 into No. 2 (do not pour No. 2 into No. 1). Add 5 cc. of $(NH_4)_2HPO_4$ reagent, shake well, let stand until clear and filter. This reagent contains about 8% of ammonium molybdate, $(NH_4)_2MoO_4$.

Ammonium Nitrate (20%).—Dissolve 200 grams of NH_4NO_3 in water and make up to 1 liter.

Ammonium Oxalate (4%).—Dissolve 40 grams of $(NH_4)_2C_2O_4 \cdot H_2O$ in water and make up to 1 liter.

NOTE.—The percentage strength of this solution refers to the crystallized salt and not to the actual content of $(NH_4)_2C_2O_4$. This note also applies to other reagents, here given, which are made from chemicals containing water of crystallization.

Ammonium Phosphate (10%).—Dissolve 100 grams of $(NH_4)_2HPO_4$ in water and dilute to 1 liter.

Ammonium Sulfate (25%).—Dissolve 250 grams of $(NH_4)_2SO_4$ in water and dilute to 1 liter.

Ammonium Sulfide (*Colorless*).—Pass H_2S gas into 750 cc. of conc. NH_4OH until saturated. Then add 500 cc. more of conc. NH_4OH and 1000 cc. of water.

Ammonium Polysulfide (*Yellow*).—Make up a bottle of colorless $(NH_4)_2S$ as above, add to it 50–75 grams of powdered sulfur, and shake.

Barium Chloride (10%).—Dissolve 100 grams of $BaCl_2 \cdot 2H_2O$ in water and dilute to 1 liter.

Barium Hydroxide (5%).—Dissolve 50 grams of $Ba(OH)_2 \cdot 8H_2O$ in water and dilute to 1 liter.

Calcium Chloride (10%).—Dissolve 100 grams of $CaCl_2 \cdot 6H_2O$ in water and dilute to 1 liter.

Calcium Hydroxide (*Lime Water*).—Make a saturated solution of $Ca(OH)_2$ and keep tightly stoppered. Decant or filter before use.

Fehling's Copper Solution (*Soxhlet Modification*).—Dissolve 69.28 grams of $CuSO_4 \cdot 5H_2O$ in water, dilute to 1 liter and filter through prepared asbestos.

Fehling's Alkaline Tartrate Solution (*Soxhlet Modification*).—Dissolve 346 grams of Rochelle salts (NaK tartrate) and 100 grams of NaOH in water and dilute to 1 liter; let stand for two days and filter through prepared asbestos.

NOTE.—The two above solutions are also used in the Munson and Walker Method.

Fehling's Copper Solution (*Allihn's Modification*).—Same as Soxhlet modification.

Fehling's Alkaline Tartrate Solution (*Allihn's Modification*).—Dissolve 346 grams of Rochelle salts and 250 grams of KOH in water and dilute to 1 liter.

Ferric Chloride (10%).—Dissolve 100 grams of $FeCl_3 \cdot 6H_2O$ in water and dilute to 1 liter.

Hydrochloric Acid, Conc. (sp. gr. 1.18–1.19).—This reagent contains 35.5–37.5% of HCl by weight.

Hydrochloric Acid, Dilute (sp. gr. 1.12).—Mix 500 cc. of conc. HCl with 400 cc. of water. The solution contains about 20% of HCl by weight.

Lead Acetate, Basic.—Boil for 0.5 hour 430 grams of normal lead acetate, 130 grams of litharge (PbO) and 1 liter of water. Let cool and settle. Dilute the supernatant liquid to sp. gr. 1.25 (at room temperature) with freshly boiled water.

NOTE.—U. S. P. lead subacetate solution may also be used in place of the above solution.

Lead Acetate, Normal (10%).—Dissolve 100 grams of $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ in water and dilute to 1 liter.

Magnesium Ammonium Chloride (*Magnesia Mixture*).—Dissolve 90 grams of $MgCl_2 \cdot 6H_2O$ (or 45 grams of anhydrous $MgCl_2$) and 240 grams of NH_4Cl in 1 liter of water, and add 50 cc. of conc. NH_4OH. Ten cc. of this solution will precipitate about 0.25 gram of H_3PO_4 or 0.18 gram of P_2O_5.

Magnesia Wash Solution (for washing magnesium ammonium phosphate precipitate).—Dissolve 100 grams of NH_4NO_3 in water, add 335 cc. of conc. NH_4OH, and dilute to 1 liter.

Mercuric Chloride (5%).—Dissolve 50 grams of $HgCl_2$ in water and dilute to 1 liter.

Nitric Acid, Conc. (sp. gr. 1.42).—This reagent contains 69–70% of HNO_3.

Nitric Acid, Dilute (sp. gr. 1.20).—Dilute 400 cc. of conc. HNO_3 with 600 cc. of water. This reagent contains about 32% of HNO_3.

Nitric Acid, Red Fuming (sp. gr. 1.80).—This is conc. HNO_3 saturated with nitrogen peroxide. (Not to be made up in the laboratory.)

Phosphoric Acid, Syrupy (sp. gr. 1.71).—This reagent contains 85% of H_3PO_4.

Potassium Bichromate (4%).—Dissolve 40 grams of $K_2Cr_2O_7$ in water and dilute to 1 liter.

Potassium Ferricyanide (1%).—Dissolve 10 grams of $K_3Fe(CN)_6$ in water and dilute to 1 liter.

Potassium Ferrocyanide (1.5%).—Dissolve 15 grams of $K_4Fe(CN)_6 \cdot 3H_2O$ in water and dilute to 1 liter.

Potassium Sulfocyanate (*Thiocyanate*) (1%).—Dissolve 10 grams of KSCN in water and dilute to 1 liter.

Silver Nitrate (2.5%).—Dissolve 25 grams of crystallized $AgNO_3$ in water and dilute to 1 liter. The solution should be kept in dark-colored glass-stoppered bottles.

Sodium Carbonate (15%).—Dissolve 150 grams of anhydrous Na_2CO_3 in water and dilute to 1 liter. It is best not to keep it in a glass-stoppered bottle. (Use a clean rubber stopper.)

Sodium Hydroxide (10%).—Dissolve 100 grams of NaOH (electrolytic) in water and dilute to 1 liter. It should be kept in a bottle stoppered with a clean rubber stopper and not exposed to the air any more than necessary.

Sodium Phosphate (10%).—Dissolve 100 grams of $Na_2HPO_4 \cdot 12H_2O$ in water and dilute to 1 liter.

Sulfuric Acid, Conc. (sp. gr. 1.84, or 66° Bé.).—This reagent contains about 94% of H_2SO_4.

Sulfuric Acid, Dilute.—Into 800 cc. of water pour cautiously 200 cc. of conc. H_2SO_4, with constant stirring. This solution contains about 30% of H_2SO_4.

Wijs Solution for Iodine Number.—Dissolve 13 grams of resublimed iodine in 1000 cc. of pure glacial acetic acid. Titrate 25 cc. with 0.1 N thiosulfate. Remove another 25 cc. to a small flask. Pass washed and dried chlorine gas into the main volume until the original thiosulfate titration is just doubled. Then add the small amount of original solution to neutralize any possible free chlorine.

Preserve in amber-colored glass-stoppered bottles sealed with paraffin until ready for use.

NOTES.—(1) Moisture spoils Wijs Solution. The chlorine must be passed through a washing bottle containing water and then through two bottles each containing conc. H_2SO_4.

(2) In making the check titrations after passing the Cl into the solution, pipette out 25 cc., add 40 cc. of 10% KI solution and 75 cc. of water and titrate with 0.1 N thiosulfate until colorless. If the vessel containing the solution is placed over a white surface, the end-point is very sharp without adding any starch indicator.

STANDARD VOLUMETRIC SOLUTIONS

General.—The solutions which are to be kept in stock for general laboratory use are the following:

0.5 N Hydrochloric Acid
0.1 N Hydrochloric Acid
0.1 N Potassium or Sodium Hydroxide
0.1 N Oxalic Acid

0.1 N Potassium Permanganate
0.1 N Sodium Thiosulfate
0.1 N Iodine
0.1 N Potassium Bichromate
0.1 N Silver Nitrate
0.1 N Sulfocyanate
0.1 N Arsenious Acid

In making up standard solutions all weighings must be made with standardized weights and all volumetric apparatus (pipettes, burettes, and flasks) must have been calibrated carefully at 20° C. In titrating standard solutions the burettes should be allowed to drain at least 3 minutes before checking the reading and proper calibration corrections must be made.

It is not necessary to have the solutions precisely 0.1 or 0.5 normal, provided the exact strength is known. The strength of the solution is expressed in terms of a "factor." This "factor" is the ratio between a given number of cc. of the solution in question and the number of cc. of a theoretically correct solution. In other words, if 50 cc. of a given solution of NaOH are neutralized by 45 cc. of exactly 0.1 N HCl, then the NaOH solution has a factor of 0.900, which is obtained by dividing 45 by 50. In using factor solutions the number of cubic centimeters of the solution in question used in titrating, multiplied by its factor, gives the corresponding number of cc. of a solution of correct strength.

All standard solutions for the laboratory are to be made up at 20° C. or made up at a known temperature and the "factors" corrected to 20° C. (A table of corrections is given on p. 13.) The "factors" of these solutions should in no case be greater than 1.005 or less than 0.995. The factor of each solution should be determined at intervals not exceeding 1 month and the figures entered in a record book kept for that purpose and also on the label of the bottle. Each solution should be titrated by two chemists independently and their results must agree satisfactorily and be accepted before the solution is released for use.

0.5 N Hydrochloric Acid.—(18.233 grams hydrogen chloride per liter or about 43.0 cc. of conc. HCl, sp. gr. 1.20.)

STANDARDIZATION.—Make up the desired amount of solution, mix *thoroughly* and standardize against pure Na_2CO_3.

The sodium carbonate is best prepared by heating sodium bicarbonate* of the highest purity by one of the following two methods:

I. Half fill a platinum dish with pure powdered $NaHCO_3$, place it in an air bath already heated to about 200° C. and raise the temperature to 270–280° (never more than 300°). Let remain at this temperature 0.5 hour, then cool in a desiccator and, before quite cold, transfer to a warm, dry, stoppered tube or bottle, out of which it may be weighed rapidly when wanted. For each standardization of 0.5 N acid weigh out accurately about 1.1 grams of the resulting Na_2CO_3

II. Accurately weigh a platinum crucible and place in it about 1.75 grams of pure $NaHCO_3$. Place in an asbestos disc with a hole cut in it which will admit the crucible to about half its depth. Cover the crucible and heat at a temperature which will just give a very dull red on the bottom. Continue the heating for at least 0.5 hour, cool in a desiccator and weigh accurately the resulting Na_2CO_3.

After the Na_2CO_3 is prepared (it should be anhydrous and free from lumps), dissolve the accurately weighed portion in about 100 cc. of water, add 2 drops of methyl orange and titrate with the acid to the point where the color changes from yellow to pinkish orange. For very accurate work the end-point should be matched against the color of 100 cc. of distilled water saturated with CO_2 and containing 2 drops of methyl orange solution.

Calculation.—1 gram of pure Na_2CO_3 is equivalent to 37.736 cc. 0.5 N acid.

If A = weight of Na_2CO_3 taken,

B = cc. of HCl (titration),

and F = the factor of the solution;

then $F = \frac{37.736\,A}{B}$.

The solution should be so made up that F is greater than 1. Add the required amount of distilled water to make the solution exactly 0.5 N, mix thoroughly and restandardize the fresh solution as above.

* The sodium bicarbonate used for this purpose should be used for no other. Before use it must be carefully tested and its purity ascertained. The bottle should then be labeled "for standardizing purposes only."

EXAMPLE.—If the factor is 1.042, then for each liter of the solution there should be added 42 cc. of water.

Optional Method.—Pipette 25 cc. of the acid into an Erlenmeyer flask and add an excess of $CaCO_3$ to neutralize the acidity. Add a few drops of K_2CrO_4 or Na_2CrO_4 indicator solution, titrate with 0.1 N $AgNO_3$ solution to the appearance of a reddish color and note the exact amount of the $AgNO_3$ required. To another 25-cc. portion of the acid add the amount of 0.1 N $AgNO_3$ found by the previous titration and 1 drop in excess. Heat to boiling and let stand, protected from the light, until the AgCl settles clear. Filter on a Gooch crucible, previously heated to 140–150° C. and weighed; wash with hot water, testing the filtrate to make sure of an excess of $AgNO_3$. Dry the AgCl at 140–150° C., cool and weigh. Or, place the Gooch crucible in a larger platinum crucible and heat over a flame until the edges of the AgCl just *begin* to fuse; then cool and weigh.

CALCULATION.

Let A = weight of AgCl equivalent to 25 cc. of exactly 0.5 N HCl = 1.7917 gram;

B = weight of AgCl found;

and F = factor of the solution.

Then $F = \frac{B}{1.7917}$.

0.1 N Hydrochloric Acid.—(3.647 grams hydrogen chloride per liter or about 8.45 cc. of conc. HCl.)

STANDARDIZATION.—Follow the same method as for 0.5 N HCl; dissolve about 1 gram of Na_2CO_3 (accurately weighed) in 500 cc. of water in an accurate volumetric flask, pipette out 100 cc. of this diluted solution with an accurate pipette and titrate with the 0.1 N HCl.

0.1 N Caustic.—(5.610 grams KOH or 4.001 grams NaOH per liter. Weigh out about 5.8 grams of stick KOH or 4.2 grams of stick NaOH for each liter of solution.)

STANDARDIZATION.—Pipette out 50 cc. of the solution and titrate against 0.1 N HCl, using 2 drops of methyl orange indicator. Titrate a second 50-cc. portion with phenolphthalein indicator. The factor for *each* indicator should be written on the bottle. The factor is obtained by multiplying the factor of the

0.1 N HCl by the number of cc. of the latter used in titration and dividing by 50 the figure thus obtained.

0.1 N Oxalic Acid.—(6.302 grams $H_2C_2O_4 \cdot 2H_2O$ per liter.)

STANDARDIZATION.—Pipette out 50 cc. of the solution and titrate with 0.1 N caustic and phenolphthalein. Multiply the number of cc. of 0.1 N caustic used in the titration by its phenolphthalein factor and divide by 50 to obtain the factor of the solution.

NOTE.—This solution may also be standardized against 0.1 N $KMnO_4$ solution. It should be kept in a dark-colored bottle away from light.

0.1 N Potassium Permanganate.—(3.161 grams $KMnO_4$ per liter.)

NOTE.—The $KMnO_4$ should be dissolved in a small amount of distilled water and filtered through glass wool or a Gooch crucible with an asbestos mat before diluting to proper volume. This solution should be kept in a dark-colored bottle away from light.

STANDARDIZATION.—Weigh out accurately 6.700 grams of pure, freshly dried sodium oxalate. Dissolve in 250–300 cc. of hot distilled water. Transfer to a liter volumetric flash and make up to volume at 20° C. This solution will be exactly 0.1 N.

Pipette out 50 cc. of the above solution into an Erlenmeyer flask. Add 5 cc. of conc. H_2SO_4 and heat to boiling. Titrate immediately with the $KMnO_4$ solution, adding the latter drop by drop at first. The first appearance of a faint but permanent pink color is taken as the end-point. To obtain the factor of the $KMnO_4$ solution, divide 50 cc. by the number of cc. of $KMnO_4$ required for the titration.

First Optional Method.—Pipette out 50 cc. of 0.1 N oxalic acid solution and add 50 cc. of distilled water and 5 cc. of conc. H_2SO_4; heat to boiling and titrate with the $KMnO_4$ solution until a permanent pink color forms. Multiply the factor of the 0.1 N oxalic acid solution by 50 and divide by the number of cc. of $KMnO_4$ used, to obtain the factor of the latter.

Second Optional Method.—Weigh out 1.9607 grams of pure ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. Dissolve in 100 cc. of distilled water, add 5 cc. of conc. H_2SO_4, cool and titrate immediately with the $KMnO_4$ solution until a permanent pink

color is formed. The factor is obtained by dividing 50 by the number of cc. of $KMnO_4$ solution used.

0.1 N Sodium Thiosulfate.—(24.820 grams $Na_2S_2O_3 \cdot 5H_2O$ per liter.)

STANDARDIZATION.—Standardize the solution against 0.1 N $K_2Cr_2O_7$ solution as follows: Weigh out accurately 4.9035 grams of C. P., freshly dried $K_2Cr_2O_7$, dissolve in about 200 cc. of distilled water and make up to volume in a liter volumetric flask at 20° C. This will make a 0.1 N solution. Place in a 350-cc. glass-stoppered bottle 100 cc. of distilled water and 30 cc. of 10% KI solution. Then add from an accurate pipette 50 cc. of the above bichromate solution followed by about 7 cc. of conc. HCl. Shake and let stand for 3 minutes. Cool under the tap so that when the stopper is removed any adhering liquid will be sucked in. Wash the stopper carefully, and titrate the contents of the bottle with thiosulfate solution. When the yellow color of iodine has almost disappeared, add about 1 cc. of starch solution and continue the titration until the deep blue color of the solution changes to sea-green. By conducting the titration carefully this change should be brought about by a single drop of thiosulfate solution.

Divide the number of cc. of bichromate solution taken (*i.e.* 50 cc.), by the number of cc. of thiosulfate required for the titration. The quotient will be the factor of the 0.1 N thiosulfate.

0.1 N Iodine.—(12.693 grams sublimed iodine per liter.)

NOTE.—This solution should be kept in a dark-colored bottle away from light.

Weigh out 12.7 grams of iodine for each liter of solution. Also weigh out (for each liter) 20–25 grams of pure KI and dissolve in as little water as possible. Then add the iodine and after it has dissolved make up to the proper volume.

STANDARDIZATION.—Pipette out 50 cc. of 0.1 N thiosulfate solution and titrate with the iodine solution, using starch indicator, until a permanent blue color forms. In this case the starch may be added directly at the beginning of the titration. The factor is obtained by multiplying the factor of the 0.1 N thiosulfate solution by 50 and dividing the result by the number of cc. of iodine solution required for titration.

0.1 N Potassium Bichromate.—(4.9035 grams $K_2Cr_2O_7$ per liter.)

NOTE.—This salt can be obtained in very pure condition and when made up accurately should give a 0.1 N solution.

STANDARDIZATION.—Pipette 50 cc. of the solution into a 350-cc. glass-stoppered flask or bottle; add 150 cc. of water and 5 cc. of conc. H_2SO_4 and after cooling thoroughly add 25 cc. of 10% KI solution. Stopper the flask and let stand 10 minutes, then titrate the iodine set free with 0.1 N thiosulfate solution, using starch indicator but not adding it until the yellow color of the iodine has nearly disappeared. The end-point is denoted by the change in color of the solution from deep blue to light green. The factor is obtained by multiplying the number of cc. of thiosulfate solution used by its factor and dividing the result by 50.

0.1 N Silver Nitrate.—(16.989 grams $AgNO_3$ per liter.)

STANDARDIZATION.—Pipette out 25 cc. of the solution, dilute to about 250 cc., add a slight excess of dil. HCl and let stand until clear. Filter the AgCl on a weighed Gooch crucible; wash with an extremely dilute solution of HCl, and finally once with cold distilled water. Dry at 110° C. Place the Gooch crucible in a large platinum crucible and ignite gently until the edges of the precipitate *just begin to fuse*. Cool and weigh the AgCl.

The factor of the solution is obtained by dividing the weight of AgCl found by 0.3584.

0.1 N Sulfocyanate.—(9.717 grams KSCN or 7.611 grams NH_4SCN per liter.)

STANDARDIZATION.—Pipette 50 cc. of 0.1 N $AgNO_3$ solution into a white porcelain dish and add 100 cc. of water, 5 cc. of dil. HNO_3 and 5 cc. of ferric nitrate solution. The latter should be approximately a 10% solution and *free from chlorides* (see p. 12). Titrate with 0.1 N sulfocyanate solution until a permanent red coloration of the liquid appears. (This is best seen by artificial light.) The factor is obtained by multiplying the factor of the 0.1 N $AgNO_3$ solution by 50 and dividing the product by the number of cc. of sulfocyanate solution required in the titration.

0.1 N Arsenious Acid.—(4.948 grams As_2O_3 per liter.) Dissolve 4.96 grams of the purest sublimed As_2O_3 powder in about 250 cc. of distilled water in which has been dissolved about 20

grams of pure Na_2CO_3. The mixture needs warming and shaking for some time in order to complete the solution. When the solution is clear, cool and make up to 1 liter at 20° C.

STANDARDIZATION.—Pipette out 50 cc. into a beaker, dilute with 100 cc. of distilled water and titrate with 0.1 N iodine, using starch indicator. The starch should not be added, however, till near the end of the titration. The factor is obtained by multiplying the number of cc. of 0.1 N iodine solution used by its factor and dividing the product by 50.

INDICATORS

The following indicator solutions should be kept in stock:

Methyl Orange, Methyl Red, Phenolphthalein, Starch, Potassium or Sodium Chromate, Ferric Nitrate.

These are to be made up as follows:

Methyl Orange.—Dissolve 1 gram in distilled water and dilute to 1 liter.

Methyl Red.—Dissolve 1 gram in 100 cc. of 95% alcohol.

Phenolphthalein.—Dissolve 5 grams in 500 cc. of 50% alcohol. Since this solution will be slightly acid, it must be neutralized by adding 0.01 N alkali cautiously till a faint pink color appears, then just removing the color with a drop or two of 0.01 N acid.

Starch.—Triturate 5 grams of arrowroot starch with a little cold water and then add, with constant stirring, 1000 cc. of boiling water. Set aside to cool and then decant, or better filter. Add 2 cc. of Oil of Cassia or of $CHCl_3$ as a preservative.

NOTE.—So-called "soluble starch" must not be used as an indicator.

Potassium or Sodium Chromate.—Dissolve 25 grams of K_2CrO_4 or 21 grams of Na_2CrO_4 in a small amount of distilled water. Add a drop or two of $AgNO_3$ solution to remove any chloride (sufficient $AgNO_3$ must be added to form a *brick-red* precipitate), filter and dilute to 250 cc.

Ferric Nitrate.—Dissolve 10 grams of $Fe(NO_3)_3 \cdot 9H_2O$ in distilled water, add a few drops of dil. HNO_3 and make up to about 100 cc. A portion of this solution should be tested with $AgNO_3$ solution to make sure that it contains no chloride.

NOTE.—Instead of ferric nitrate, the solution may be made up from ferric alum, $Fe_2(NH_4)_2(SO_4)_4 \cdot 24H_2O$. To this solution should be added a little

TABLE I—CONVERSION OF THE APPARENT VOLUME OF H_2O OR OF A 0.1 N SOLUTION AS READ IN GLASS AT T° TO ITS VOLUME AT 20° C.

	Corrections to be Added in cc.					Corrections to be Subtracted in cc.									
Vol. cc.	15°	16°	17°	18°	19°	21°	22°	23°	24°	25°	26°	27°	28°	29°	30°
5	.004	.003	.002	.002	.001	.001	.002	.003	.004	.005	.006	.007	.009	.010	.011
10	.008	.006	.005	.003	.002	.002	.004	.006	.008	.010	.012	.015	.018	.020	.023
15	.011	.009	.007	.005	.003	.003	.006	.009	.012	.015	.019	.022	.028	.030	.034
20	.015	.013	.010	.007	.004	.004	.008	.012	.016	.020	.025	.030	.035	.040	.046
25	.018	.016	.012	.008	.004	.004	.009	.014	.020	.025	.031	.037	.044	.050	.057
30	.023	.020	.015	.010	.005	.005	.011	.017	.024	.029	.037	.045	.053	.061	.069
35	.027	.022	.017	.012	.006	.006	.013	.020	.028	.034	.044	.052	.062	.071	.080
40	.030	.025	.020	.014	.007	.007	.015	.023	.032	.039	.050	.060	.070	.081	.092
45	.034	.028	.022	.015	.008	.008	.017	.026	.036	.046	.056	.067	.079	.091	.103
50	.038	.031	.024	.017	.009	.009	.019	.029	.040	.051	.063	.075	.088	.101	.115
100	.076	.063	.049	.034	.018	.018	.038	.058	.080	.102	.126	.150	.176	.202	.229

In using burettes all corrections may be rounded off to the nearest 0.01 cc., whereas the next decimal place should be used in accurate work with pipettes smaller than 25 cc. For Normal Solutions the above corrections should be increased by 50% and for 0.5 N Solutions by 25%.

conc. HNO_3. It should be kept in an amber-colored bottle and not exposed to the air.

REFERENCE.—Sutton: "Volumetric Analysis."

CALIBRATION OF VOLUMETRIC GLASSWARE AND ANALYTICAL WEIGHTS

General.—The basic factor in the accuracy of quantitative analytical procedures is the accuracy of the volumetric glassware and of the weights employed. The standard liter is the volume of 1 kg. of pure water at 4° C. weighed in vacuum. It is not

TABLE II—CORRECTIONS FOR DETERMINING TRUE CAPACITIES OF GLASS VESSELS FROM THE WEIGHT OF WATER IN AIR
(Bureau of Standards, *Circular* 19)
Indicated Capacity 1 Liter
(Amounts to be added to apparent weight of water in grams to obtain actual capacity in cc. at 20° C.)

Temperature °C.	*Tenths of Degrees*									
	0	1	2	3	4	5	6	7	8	9
15	2.07	2.08	2.10	2.11	2.12	2.14	2.15	2.16	2.17	2.19
16	2.20	2.21	2.23	2.24	2.25	2.27	2.28	2.29	2.31	2.32
17	2.34	2.35	2.37	2.38	2.40	2.41	2.43	2.44	2.46	2.47
18	2.49	2.50	2.52	2.54	2.55	2.57	2.58	2.60	2.62	2.63
19	2.65	2.66	2.68	2.70	2.72	2.73	2.75	2.77	2.79	2.80
20	2.82	2.84	2.86	2.87	2.89	2.91	2.93	2.95	2.96	2.98
21	3.00	3.02	3.04	3.06	3.08	3.10	3.12	3.13	3.15	3.17
22	3.19	3.21	3.23	3.25	3.27	3.29	3.31	3.33	3.35	3.38
23	3.40	3.42	3.44	3.46	3.48	3.50	3.52	3.54	3.57	3.59
24	3.61	3.63	3.65	3.67	3.70	3.72	3.74	3.76	3.79	3.81
25	3.83	3.85	3.88	3.90	3.92	3.95	3.97	3.99	4.02	4.04
26	4.06	4.09	4.11	4.14	4.16	4.18	4.21	4.23	4.26	4.28
27	4.30	4.33	4.35	4.38	4.40	4.43	4.45	4.48	4.51	4.53
28	4.56	4.58	4.62	4.63	4.66	4.69	4.71	4.74	4.76	4.79
29	4.82	4.84	4.87	4.90	4.92	4.95	4.98	5.01	5.03	5.06

For flasks larger or smaller than 1 liter use proportionate corrections.

convenient to work at 4° C., however, and the generally accepted standard temperature for the use of volumetric glassware in this country is 20° C. The true volume of a glass vessel at 20° C. may be calculated from the weight (in air with brass weights) of the water which it contains at 20° C. Table II gives sufficient data for ordinary work. For extreme accuracy the original *Circular* should be consulted.

Volumetric Ware. *Flasks.*—Clean the flask with chromic acid cleaning solution, wash with distilled water, dry and weigh at room temperature. Then fill to the mark with water and weigh again. Take the temperature of the water and calculate the corresponding volume at 20° C. from the table. With flasks of 200-cc. or smaller, weigh to the second decimal place; with larger flasks the first decimal place is sufficient.

NOTE.—If the weight of the flask filled with water is greater than the capacity of the balance, the contents of the flask may be ascertained by means of calibrated pipettes and burettes, using water at 20° C.

Pipettes.—The time of delivery for a pipette is generally marked upon it. If not, the time may be arbitrarily chosen, depending upon the size of the pipette, within the limits of the following table, and etched upon the bulb.

TABLE III—DELIVERY TIME FOR PIPETTES

Size of Pipette, *Cubic Centimeters*	Time of Delivery, *Seconds*
10 or less	12–15
10–50	15–20
50–100	20–30
100 or more	30–40

In calibrating, clean the pipette thoroughly with chromic acid cleaning solution, rinse free from acid, fill with water to the upper mark, and let the water run out into a weighed Erlenmeyer flask. At the end of the time specified for delivery (figured from the time the water is released), touch the tip of the pipette to the liquid and immediately withdraw it.

The Erlenmeyer flask should be as small as possible and should be weighed immediately to avoid loss by evaporation.

In the case of small pipettes, the water should be at exactly 20° C. when delivered. For pipettes of 25 cc. or larger, determine the temperature of the water immediately after weighing and correct to the corresponding volume at 20° C.

Burettes.—Calibrate burettes by the Ostwald pipette, Fig. 1. Attach this to the tip of the burette, or in the case of a side-arm burette, to the side-arm, with a pinch-cock between the pipette and the burette. Also attach an outlet tube by a rubber connection with a pinch-cock to the bottom of the pipette. Clean the burette thoroughly and fill with water some distance above the upper mark. Clamp the burette and pipette in such a way that they remain rigid during the calibration. Let the water run from the burette into the pipette by means of the pinch-cock, making sure no air bubbles are present. Set the water in the burette at the zero point and the water in the pipette at the lower mark. The apparatus is now ready to make the calibration.

FIG. 1. Ostwald Calibrating Pipette.

Let water run from the burette into the pipette to the upper mark. Then draw it off to the lower mark of the pipette. Take the reading of the burette and repeat the operation until the water is nearly at the end of the graduations of the burette, noting accurately the burette reading each time the pipette is filled. Then again fill the burette to the zero mark with water and draw off the water down to the last reading obtained during the calibration, catching the water in a small weighed Erlenmeyer flask and letting the burette drain 3 minutes before making the final adjustment. The water in the burette should be at 20° C. or at a known temperature so that its volume may be corrected to 20° C.

Divide the volume of the water at 20° C. by the number of times the pipette was filled. This will give the capacity of the pipette, which should be calculated to three decimal places. Suppose this to be 2.001 cc., then the difference between the successive readings of the burette and the successive numbers 2.001, 4.002, 6.003, etc., gives the error in the graduations of the burette at these intervals. Each burette should be numbered and its correction tabulated, or plotted as a curve, showing + or − corrections at each even cc. mark.

Analytical Weights.—The simplest way to calibrate a set of weights is to compare each weight directly with the corresponding weight from a set of standard weights which are known to be correct. It may happen, however, that the majority of the weights in a given set would require a correction by this process, whereas their ratio one to another in the same set is correct. Such a set may be calibrated merely by getting an accurate comparison between the different weights. The most satisfactory procedure is T. W. Richards' Method of Substitution.*

The weights to be standardized are weighed wholly on one side of the balance, the comparison being made by substitution. It is necessary that all of the fractional weights taken together should constitute a gram and during the calibration it is convenient to add an extra centigram weight from another set. The different weights of the same denomination should be marked for easy identification and should always be arranged in the same order in the box.

Place one of the centigram weights on the left-hand scale pan and balance it by any suitable tare. A set of crude weights is the most convenient tare and a 5-mg. weight may be kept on the left-hand pan during the entire calibration so as to bring the rider into a convenient position. Bring the balance to the correct zero point by moving the rider. Then substitute another centigram weight for the first. The amount by which the rider must be moved to the right or the left to attain the same equilibrium gives at once the positive or the negative difference between the two weights. In this way, compare every weight with every other weight of the same denomination as well as with the combination of all the smaller weights.

By assuming that any one of the weights is correct it is possible to calculate the positive or negative corrections to be applied to the other weights to make the ratio correct between all the weights. It is generally most convenient to take the centigram weight as correct for preliminary calculations. From it, simply by adding or subtracting, arrange a table showing the values of all the other weights in terms of the original centigram weight. These values are usually far too different from the face values of the weights for convenient use, because the assumed

* *J. Am. Chem. Soc.*, **22**, 144 (1900).

standard is so small. They may be brought to a more convenient basis by dividing each value by the value of one of the larger weights (the 10-gram weight is usually suitable). This is most conveniently done by comparing each weight with the corresponding aliquot value of the weight taken as a final standard. The difference between the actual value and the ideal value will then give a correction to be applied to the weight, negative if the weight is not heavy enough and positive if it is too heavy. Table IV shows an example of the calibration of a set of weights up to 10 grams.

TABLE IV—DATA FOR CALIBRATION OF WEIGHTS

Nominal Values	Data Obtained by Substitution Method, Grams	Preliminary Values (Actual), Grams	Aliquot Parts of 10.01768 (Ideal), Grams	Corrections (Actual Minus Ideal)
(0.01)	= Standard of comparison	Standard	0.01002	−0.00002
(0.01′)	= (0.01) +0.00006	0.01006	0.01002	+0.00004
(0.01″)	= (0.01′) −0.00001	0.01005	0.01002	+0.00003
(0.02)	= (0.01) + 0.01′ − 0.00001	0.02005	0.02004	+0.00001
(0.05)	= (0.02) + etc. − 0.00007	0.05009	0.05009	0.00000
(0.1)	= (0.05) + etc. − 0.00006	0.10019	0.10018	−0.00001
(0.1′)	= (0.1) + 0.00001	0.10020	0.10018	+0.00002
(0.2)	= (0.1) + (0.1′) − 0.00004	0.20035	0.20035	0.00000
(0.5)	= (0.2) + etc. − 0.00011	0.50088	0.50088	0.00000
(1)	= (0.5) + etc. − 0.00004	1.00183	1.00177	+0.00006
(1′)	= (1) − 0.00002	1.00181	1.00177	+0.00004
(1″)	= (1) − 0.00006	1.00177	1.00177	0.00000
(2)	= (1′) + (1″) + 0.00025	2.00383	2.00354	−0.00029
(5)	= (2) + etc. − 0.00040	5.00884	5.00884	0.00000
(10)	= (5) + etc. − 0.00040	10.01768	10.01768	Standard

If the corrections are significant, prepare a table showing at once the corrections corresponding to the usual combinations of weights from 0.01 to 0.99 gram and from 1 gram upwards.

NOTES.—(1) The question of positive and negative corrections is sometimes confusing. If a given weight is not heavy enough, its correction is negative since its deficiency in weight necessitates the addition of extra weight on the rider-arm and hence the sum of the face values of all the weights used is too large.

(2) If any of the larger weights is found seriously off, it should be corrected by unscrewing the top and adding or removing weight as required. Then recalibrate the adjusted weight.

CARE OF PLATINUM

Cleaning Platinum Ware.—Every careful analyst necessarily uses clean apparatus. The habit of cleaning and polishing platinum dishes and crucibles immediately after using is easily formed and repays the user with increased confidence in his work as well as in the prolonged life of the article.

Rubbing the surface of platinum with moist sea sand (round grains only), applied with the fingers, will remove most impurities and polishes the metal without appreciable loss.

Fusing potassium bisulfate or borax in the dish and then boiling in water and polishing as above with sand gives a clean bright surface. When it is desired to clean the outer surface of dishes in this manner, they must be placed in dishes of sufficient size to allow the fused flux to envelop completely the article to be cleaned.

Sodium amalgam possesses the property of wetting platinum without amalgamating with it, even when other metals are purposely added to the amalgam. This substance is, therefore, useful for effecting a quick and thorough cleansing of platinum. The amalgam is gently rubbed upon the metal with a cloth and then moistened with water, which oxidizes the sodium and leaves the mercury free to alloy with foreign metals. The mercury is then wiped off and the dish cleaned and polished with sand, as above described.

Stains may often be removed from platinum ware by heating to redness and then dropping into the dish a pinch of dry NH_4Cl.

If the existence of a base metal alloyed with the platinum is suspected, immerse the article in question first in boiling HCl for a few minutes, then, after thorough rinsing with clean water, immerse in boiling HNO_3 free from chlorine. If the dish is unaffected in weight or appearance, and the acid baths fail to

give reaction for the base metals, their absence in appreciable quantities is assured.

Notes upon the Use and Care of Platinum Ware.—It is important to remember that, although platinum is not oxidized in the air at any temperature, nor attacked by any single acid, there are many substances that attack and combine with it at comparatively low temperatures.

The caustic alkalies, the alkaline earths, nitrates and cyanides, and especially the hydroxides of barium and lithium, attack platinum at a red heat, although the alkaline carbonates have no effect at the highest temperatures. Sulfur, in the absence of alkalies, has no action, but phosphorus and arsenic attack platinum when heated with it.

The ignition in a platinum crucible of precipitated ammonium magnesium phosphate in contact with carbon derived from the filter paper, especially when the precipitate has not been perfectly dried, is likely to result in the reduction of sufficient phosphorus to render the platinum very brittle. Similar results attend the ignition of phosphates in general in the presence of reducing agents, and great care should therefore be taken in this respect, since a very small phosphorus content may ruin platinum ware.

Platinum in spongy or finely divided form is energetically attacked by fused sodium peroxide, and platinum crucibles withstand but few fusions of this compound.

Contact with compounds of the easily reducible metals is especially dangerous at high temperatures, as alloys with platinum having a low fusing point are readily formed. This is especially true of lead.

Direct contact of platinum with burning charcoal should be avoided, since the silicon reduced from the charcoal ash unites with platinum, making it brittle and easily cracked.

Heating a platinum crucible with alcohol lamps is preferable to the use of ordinary gas. When gas is used, care should be taken to have the supply of air sufficient to insure complete combustion, since, with the flame containing free carbon, the platinum suffers deterioration by the formation of a carbide of platinum, which oxidizing later, blisters the metal. For this reason, also, the inner cone of a reducing flame should not come in contact with the platinum.

The effect of the Bunsen flame upon the surface of platinum exposed to its action produces the familiar gray appearance which cannot be removed except by burnishing. Platinum triangles often become gray and very brittle from the same cause. Systematic applications of moist sand to all articles affected in this way, after use, will keep them in good condition and materially prolong their life, with but a trifling loss in weight.

RECOVERY OF PLATINUM RESIDUES

If the residues consist entirely of water-soluble platinum salts, evaporate to dryness in a porcelain dish to remove alcohol and then take up in water. If the residues contain metallic platinum, asbestos shreds, or other insoluble solids, evaporate to dryness, and treat with aqua regia (1 part conc. HNO_3 and 3 parts conc. HCl) until all the platinum is in solution. Then evaporate to dryness, warm with a little dil. HCl and take up with water. Filter and wash the residue free from Pt salts, saving the filtrate.

Prepare a solution of NaOH of sp. gr. 1.2 and add to it 8% of glycerine. Heat this liquid to boiling and pour into it the clear Pt solution. This precipitates the Pt, which is washed with water, then with HCl and again with water. Dry and ignite in a porcelain crucible and weigh. Transfer to a flask and cover with water. Add aqua regia, in small amounts at a time, with continuous gentle heating on the water bath. Evaporate in a porcelain dish to a syrup. Continue to evaporate alternately with HCl and with water until no more nitrous fumes are given off. It is very important to have all HNO_3 removed. The solution is always intensely brown, due to the presence of more or less H_2PtCl_4. To convert this into H_2PtCl_6 saturate the fairly warm solution with chlorine gas until it becomes yellow. Evaporate to a syrup to remove the chlorine; dilute somewhat and filter. If there is much insoluble matter it should be filtered off, ignited and weighed, and this weight subtracted from the original weight. Then dilute the filtered solution until it contains 10 grams of Pt per 100 cc. (or if desired, it may be made up to any other known strength).

REFERENCE. Treadwell-Hall: "Analytical Chemistry," **1**, 236.

RECOVERY OF MOLYBDIC ACID FROM PHOSPHORUS DETERMINATIONS

Molybdic acid is an expensive reagent and it is possible and usually worth while to recover it from the waste residues and solutions from phosphate determinations.

Pour all such residues into a 12-liter carboy provided with a funnel and a glass tube attached to the stem reaching to within about 3 inches of the bottom. When the carboy is nearly full, add 50 grams of NH_4NO_3 dissolved in 100 cc. of water and 100 grams of Na_2HPO_4 crystals dissolved in 200 cc. of water. Mix well and let settle. Remove a portion of the clear supernatant liquid, heat it to boiling and add more Na_2HPO_4. If this forms a precipitate, return the solution to the carboy and add a further amount of the phosphate dissolved in water.

After the molybdate has been completely precipitated and allowed to stand over night, siphon off the clear liquor and discard it. Continue to add residues to the carboy until it is filled again and repeat the above operation.

After a sufficient amount of the yellow precipitate has accumulated, filter on a large Büchner funnel fitted with a filter paper and wash with a 2% NH_4NO_3 solution. Let the moist residue stand exposed to the air (protected from dust) for about 2 weeks in an open bottle or dry it in an oven. Use this dry ammonium phospho-molybdate for making up fresh molybdate solutions for phosphorus determinations. The dry compound contains 92% of pure MoO_3. In making up a fresh molybdate solution, weigh an amount of the yellow powder equivalent to the MoO_3 content desired. Dissolve in the usual amount of NH_4OH and for every 100 grams of the yellow powder add 7.5 grams of $MgCO_3$ dissolved in a minimum amount of HNO_3. Filter off the precipitate of $MgNH_4PO_4$ and use the filtrate in the usual way in making up the ammonium molybdate solution.

CHAPTER II

GENERAL INORGANIC ANALYSES

SULFUR

General.—For most routine purposes in analyzing refined sulfur or brimstone, it is customary to determine only the moisture, ash and sulfur content. The latter is generally determined by solution in CS_2 as described below. It should be remembered, however, that in impure samples there may be other substances besides sulfur soluble in CS_2 and it must also be further remembered that *sublimed* sulfur is not completely soluble in CS_2. For an accurate determination of the percentage of sulfur follow the procedure for Total Sulfur in Lime-sulfur Solution on page 80, using about 0.1 gram of finely ground material.

Moisture.—Grind the sample, weigh out 2–5 grams in a flat-bottomed dish and dry to constant weight at a temperature not exceeding 105° C. Report the loss as Moisture.

Sulfur (Soluble in Carbon Bisulfide).—Dissolve the residue from the moisture determination in CS_2. Filter through a weighed Gooch crucible with an asbestos mat, which has previously been treated with a little CS_2, and wash the residue with CS_2 and then with a little ether. Dry and weigh. Subtract from 100% the sum of the percentages of moisture and material insoluble in CS_2 and report the difference as Sulfur (soluble in CS_2).

Ash.—Weigh out 2–5 grams in a porcelain crucible; ignite, gently at first, and finally in a full Tirrill flame. Cool and weigh the ash.

Oil and Tar.—For certain uses the presence of very small amounts of oil or bituminous matter in sulfur is objectionable. The estimation cannot be carried out by simple extraction since the sulfur itself is slightly soluble and the amount of oil is generally very small (0.001–0.3%). It is possible, however, to extract all the oil with petroleum ether and then remove from the extract the soluble sulfur by means of copper foil.

Apparatus.—(*a*) 100-cc. volumetric flask.

(*b*) Two Soxhlet flasks, about 250-cc. capacity.

(*c*) Wiley continuous extractor without crucible or thimble.

(*d*) Roll up a sheet of copper foil 4 by 15 inches in such a way that a spiral is formed without contact between the surfaces. Leave a tab about $\frac{3}{8}$ inch square on one corner and punch a hole in this tab so that the coil may be lifted from the Wiley tube with a wire hook. Have this tab in the center of the coil.

Procedure.—Weigh into the 100-cc. flask 50 grams of the powdered sample, or a smaller quantity if the oil content is known to be high. Add about 50 cc. of redistilled petroleum ether, shake the contents thoroughly every half hour for several hours and let settle. Decant the solution through a filter into the Wiley extraction tube, shake the residual sulfur a second time with about 30 cc. of the solvent, let settle and filter as before. Continue washing and shaking the sulfur with fresh portions of the ether until about 175 cc. of solvent have been used or until there is sufficient to fill the tube above the copper foil.

Clean the copper coil with dil. HNO_3 wash with water, then with alcohol, dry with ether and place in the Wiley tube. Then boil the petroleum ether in the tube until all of the sulfur has been deposited on the copper as CuS. Transfer the solvent to the beaker, filtering if necessary to remove any loose CuS, and wash the coil and the tube and filter with small quantities of petroleum ether. Evaporate the solvent gently to dryness at low heat and weigh the residue, using as a counterpoise a flask of similar size and shape.

Note.—We have found that if the analysis is not desired in a hurry, the boiling may be omitted. The coil may be placed with the ether extract in a tall glass cylinder and allowed to stand at room temperature, lightly stoppered. The sulfur will generally be removed completely in 24–48 hours. It is advisable, however, to place a fresh coil in the solution and let it stand overnight to make sure all traces of sulfur have been removed.

MIXED ACID

General.—This method is for the analysis of so-called mixed acids. These are composed of sulfuric and nitric acids mixed in varying proportions according to the purpose for which the material is intended. There is also present a small amount of nitrosyl-sulfuric acid caused by interaction of the two acids.

Total Acidity.—Pipette 15 cc. of the sample into a previously weighed weighing bottle. Stopper the bottle immediately and weigh it. Immerse the bottle below the surface of about 400 cc. of water in a beaker. Grasp the bottle near the bottom with the left hand and tip it so that the stoppered end is well below the surface, then by means of a glass fork gradually loosen the stopper and let the liquid run out into the water very slowly. In this way the fumes will remain in the bottle and will gradually be absorbed by the water entering the bottle. With a little practice this can be accomplished without the loss of any fumes. If a bubble escapes and fumes appear on the surface of the water the determination must be discarded.

Finally rinse the weighing bottle into the beaker with water, transfer the entire contents of the beaker to a liter volumetric flask, dilute to the mark, mix thoroughly, pipette out 100 cc. and titrate with 0.5 N NaOH and methyl orange. Calculate the number of cc. of 0.5 N NaOH required for the total acidity of 1 gram of the sample.

Sulfuric Acid.—Weigh out from a Lunge pipette two separate portions of about 5 grams each into 6-inch porcelain evaporating dishes.* Add 5 cc. of water to each dish and evaporate on the steam bath for $\frac{1}{2}$ hour; then add 2 cc. more of water, evaporate for 20 minutes, cool and titrate at once with 0.5 N NaOH and methyl orange. This gives the total H_2SO_4. Calculate the titration required by 1 gram of the sample.

Note.—We have found that for ordinary mixed acids the evaporation of the water as above completely removes the HNO_3. This should be checked, however, by conducting an evaporation on a separate portion and testing the residue by the addition of a little diphenylamine. This should not produce any blue color. If it is impossible to remove the HNO_3 by evaporation, add about 1 gram of urea to the evaporated solution before titrating.

Nitrosyl-sulfuric Acid.—Pipette 15 cc. of the sample into about 150 cc. of water. Use for this purpose the same pipette as for

* If a Lunge pipette is not available, an ordinary 4-cc. pipette may be used. In this case deliver 4 cc. of the sample from the pipette into a weighed weighing bottle, allowing the pipette to drain for a definite number of seconds. Stopper the bottle quickly and weigh it. Then deliver two portions from the same pipette into the two evaporating dishes, allowing the pipette to drain for the same length of time in each case. In this way the same weight of sample is obtained.

the total acidity and calculate the weight of sample taken. Titrate at once with 0.1 N $KMnO_4$. This gives the Nitrosyl acid, $HNOSO_4$. Calculate the titration to a 1-gram basis.

Calculations.—Having all the titrations calculated to the basis of 1 gram of the sample, calculate the total H_2SO_4 and subtract from it the equivalent amount of H_2SO_4 in the $HNOSO_4$.

Subtract from the total acidity titration the titration for total H_2SO_4 and calculate the difference to HNO_3. Then correct this latter figure by subtracting the equivalent amount of HNO_3 in the $HNOSO_4$.

Add together the percentages of H_2SO_4, HNO_3 and $HNOSO_4$, subtract the sum from 100% and report the difference as water.

The reaction for the titration of the nitrosyl acid may be written as follows:

$$4KMnO_4+5N_2O_3+H_2SO_4=2K_2SO_4+4MnSO_4+10HNO_3+H_2O.$$

Factors.—1 cc. 0.1 N $KMnO_4$ = 0.006354 gram $HNOSO_4$.
= 0.001900 gram N_2O_3.
1 cc. 0.5 N NaOH = 0.02452 gram H_2SO_4.
= 0.03151 gram HNO_3.
$HNOSO_4 \times 0.4959 = HNO_3$.
$HNOSO_4 \times 0.2991 = N_2O_3$.
$HNOSO_4 \times 0.7718 = H_2SO_4$.

FUMING SULFURIC ACID (OLEUM)

General.—Fuming sulfuric acid or oleum consists of a solution of SO_3 in conc. H_2SO_4. From a determination of the total SO_3, the amount of free SO_3 and of H_2SO_4 can be calculated. The amount of free SO_3 varies widely—a common concentration is 18 to 25%, but it may run over 60%.

Total SO_3.—Since oleum takes up water very rapidly, great precautions must be observed in getting the sample for analysis. The most satisfactory procedure is as follows: Seal off the end of an ordinary glass tube and blow a bulb about 0.75 inch in diameter. Draw the other end out to a capillary. Cool and weigh. Warm the bulb end some distance from the flame and immerse the capillary in the oleum. With the end still immersed, cool the bulb as rapidly as possible. The contraction of air will draw the oleum up into the bulb. Remove the bulb, invert it, and seal

off the capillary end in a flame. Clean the outside of the bulb carefully and again weigh to obtain the amount of oleum which it contains. Great care must be taken in handling the bulb, as the material in it is very dangerous.

Fill a 500-cc. glass-stoppered bottle about two-thirds full of distilled water and add to it sufficient 0.5 N NaOH, carefully measured, to give a slight excess. If the oleum is assumed to contain 90 % of total SO_3, and the corresponding amount of NaOH is calculated on this basis from the weight taken, it will give a sufficient excess.

Immerse the bulb in this solution, hold it firmly against the bottom with a rubber-tipped policeman or glass stirring rod and carefully break the capillary end. Stopper the bottle and shake. Finally the bulb itself should be broken and also the tip of the capillary crushed to make sure that all the acid has come in contact with alkali. Add methyl orange and titrate the excess of NaOH with 0.5 N or 0.1 N HCl. Then transfer to a 500-cc. volumetric flask and make up to the mark with distilled water. Pipette 100 cc. into a 250-cc. beaker and add 5 cc. of 10% $BaCl_2$ solution diluted to about 50 cc. It is important that the latter be added drop by drop and that both solutions be boiling.

If possible, boil for 5 minutes and let stand overnight. The next morning reheat the solution on the steam bath and filter. If results are desired quickly, boil the solution for at least 30 minutes after adding $BaCl_2$, let settle till clear and filter. Wash with boiling water, ignite in a weighed platinum crucible, cool in air, moisten with dil. H_2SO_4, again ignite (gently at first to avoid spattering), cool in a desiccator, and weigh as $BaSO_4$. Calculate to SO_3.

Calculations.—Subtract from 100% the percentage of total SO_3 obtained by the $BaSO_4$ method. The difference is H_2O combined as H_2SO_4. Calculate this to H_2SO_4. Subtract this percentage from 100%. The difference is free SO_3. Report as follows:

Total Sulfur Trioxide, SO_3.
  Equivalent to:
    Sulfuric Acid, H_2SO_4.
    Free Sulfur Trioxide, SO_3.

Factors.—1 cc. 0.5 N NaOH = 0.020016 gram SO_3.

$BaSO_4 \times 0.3430 = SO_3$.

$H_2O \times 5.444 = H_2SO_4$.

NOTES.—(1) The titration is carried out merely as a check. Theoretically it should give the same amount of total SO_3 as the precipitation method, but generally it shows somewhat higher results. If the result for SO_3 by titration varies widely from that obtained by precipitation, the latter should be carefully checked.

(2) On account of the necessity of aliquoting and also on account of the large factor from H_2O to H_2SO_4, it is necessary to work with extreme care and, wherever possible, it is advisable to run at least five determinations and take the average.

(3) Oleum samples should always be kept in glass-stoppered bottles away from light.

(4) The freezing point of oleum depends upon the amount of free SO_3 which it contains, and analytical results can therefore be checked by determining the freezing point.

LIQUID SULFUR DIOXIDE

General.—Sulfur dioxide is a gas which can be comparatively easily liquified and is furnished commercially in the liquid form in cylinders or tubes. Its melting point is about −76° C. and it boils at −10° C. It is made by condensing and, if necessary, redistilling the gases formed by the roasting of iron pyrite, zinc blende or other sulfur-bearing minerals. It may, of course, also be made by burning sulfur.

Liquid SO_2 sold commercially today frequently has a purity of 99.8% or higher and is practically colorless. In the dry state it does not corrode. The chief impurity is water and sometimes a little H_2SO_4. Excessive amounts of water will make the material corrosive to metals and also tends to promote decomposition with the formation of H_2S and eventually of sulfur, which dissolves in the liquid and colors it yellow. The ordinary commercial grade usually contains from 0.3 to 0.5% of moisture, whereas material purified by double distillation usually contains not more than 0.1%.

The following tests are of value in ascertaining the purity of liquid SO_2:

Color.—Incline the tube so that the outlet is below the horizontal. Open the valve and let some of the liquid run into a

clean beaker. High-grade material should be colorless or not more than pale straw color.

Residue on Evaporation.—Pour 100 cc. of the liquid into a funnel tube, the lower part of which is graduated to 0.1 cc. Let the liquid evaporate spontaneously until the odor of SO_2 has disappeared. Read the volume of the residue, which consists essentially of water with any H_2SO_4 which may be present.

NOTE.—The funnel tube used in moisture determination by the Xylol Method is satisfactory for this test.

Copper Corrosion Test.—Pour 50 cc. into a clean, brightly polished, spun copper dish, such as used in the corrosion test for gasoline (see p. 235) and let it evaporate spontaneously. There should be no grey or black deposit on the copper, which would indicate the presence of H_2S.

ALKALIES

(HYDROXIDES, CARBONATES AND BICARBONATES OF SODIUM AND POTASSIUM)

General.—Mixtures of carbonates and bicarbonates or of carbonates and hydroxides of the alkalies can be analyzed by a double titration with standard acid, using phenolphthalein and methyl orange indicators. If only Na or K is present, the amounts of carbonate and hydroxide can be calculated directly; otherwise the proportions of Na and K must also be determined on a separate portion. (For the determination of potassium, see p. 61.) The method of double titration is chiefly of value for mixtures of hydroxide and carbonate containing only a small proportion of carbonate. Where the proportion of carbonate is high the barium chloride method should be used. For an accurate determination of bicarbonate use the caustic titration with $AgNO_3$ as later described.

In reporting results, the total alkalinity calculated as Na_2O (or K_2O) should be expressed, as well as the various forms of alkalinity.

In the following procedures it is assumed that the material contains K or Na, but not both, and that it contains carbonate, bicarbonate, hydroxide, carbonate and bicarbonate, or carbonate

and hydroxide. (It should be noted that bicarbonate cannot exist in the presence of hydroxide.)

Moisture.—Weigh out as large a sample as practicable, dissolve rapidly in CO_2-free water and make up to volume. Pipette an aliquot representing 1 or 2 grams into a platinum or porcelain dish. Evaporate to dryness and dry to constant weight at 105° C. Report loss as moisture.

NOTE.—In the case of soda ash (Na_2CO_3) or pearl-ash (K_2CO_3), 1–5 grams of the sample may be weighed out directly and dried to constant weight. In the case of caustic soda or potash, the moisture is generally taken "by difference," as it is very difficult to get accurate results on account of the tendency to carbonate. If bicarbonates are present, the above method cannot be used for the moisture determination, as bicarbonates will change to carbonates. In such cases the material should be heated for at least two hours at 200° C. The loss is moisture plus CO_2. From the amount of bicarbonate, separately determined, calculate the CO_2 and H_2O which it would liberate and subtract this amount from the total loss to obtain the true moisture.

CALCULATION.—$NaHCO_3 \times 0.3691 = H_2CO_3$ liberated.
$KHCO_3 \times 0.3098 = H_2CO_3$ liberated.

DETERMINATION OF THE ALKALIES

Qualitative Tests.—To test for hydroxide, dissolve a small amount of the sample in CO_2-free water, add an excess of $BaCl_2$ solution and filter rapidly. If the filtrate is alkaline to phenolphthalein, hydroxide is present. More $BaCl_2$ solution, however, should be added to the filtrate to make sure that an excess has been used. Carbonate or bicarbonate is, of course, indicated by effervescence with acid. If hydroxide is present, the material is free from bicarbonates. If hydroxide is not present, the presence of bicarbonate would be indicated in the quantitative analysis by the fact that the titration with methyl orange would be more than twice that with phenolphthalein.

Carbonate and Bicarbonate.—Dissolve a considerable amount of the sample in freshly boiled distilled water and titrate an aliquot of the solution corresponding to 1 gram (or more if necessary) directly with 0.5 N acid and phenolphthalein; then add methyl orange and complete the titration as described below under Caustic Soda. If the phenolphthalein titration is one-half the total methyl orange titration, carbonates only are present.

In case bicarbonates are present, twice the phenolphthalein titration will give normal carbonates, and the difference between the methyl orange titration and twice the phenolphthalein titration will give bicarbonate. In case carbonate alone is present, calculate the methyl orange titration direct, both as carbonate and as Na_2O or K_2O. In making calculations use the following factors:

CALCULATION.—1 cc. 0.5 N acid = 0.02000 gram NaOH.
= 0.02805 gram KOH.
= 0.02650 gram Na_2CO_3.
= 0.03455 gram K_2CO_3.
= 0.02355 gram K_2O.
= 0.01550 gram Na_2O.

NOTES.—(1) The above method is reliable only for comparatively small amounts of carbonate in the presence of caustic. For small amounts of caustic in the presence of carbonate, or for mixtures of carbonate and bicarbonate, results are only approximate (see below).

(2) In carrying out the titration it is essential to have sufficient water so that no bubbles of CO_2 are given off during the phenolphthalein titration. The acid should also be added slowly with stirring. To obtain reliable results all precautions and directions must be exactly observed.

(3) For the so-called "New York-Liverpool Test" multiply the actual percentage of Na_2O found by 1.03226 and for the "Newcastle Test" multiply the actual percentage of Na_2O by 1.013.

Analysis of Caustic Soda (or Caustic Potash).—Caustic soda and potash invariably contain a certain amount of carbonate. Carbonate and hydroxide can both be determined in one operation as follows: Dissolve a considerable amount of the sample in freshly boiled distilled water and dilute to volume, working rapidly and avoiding undue exposure, as caustic rapidly takes up moisture and CO_2.

Pipette an aliquot of the solution corresponding to about 1 gram into a 500-cc. beaker, dilute to about 450 cc., add 1 cc. of phenolphthalein solution, and with the tip of the burette beneath the surface of the solution, titrate with 0.5 N acid until the pink color just disappears. Then add 3 or 4 drops of methyl orange indicator and continue the titration to the first appearance of a permanent pink color. The first titration gives the number of cc. of acid required to neutralize all the hydroxide and half of

the carbonate, since phenolphthalein is neutral to bicarbonate. The methyl orange (total) titration gives the total alkalinity.

Let x = cc. required with phenolphthalein,
and y = cc. required with methyl orange;
then $2(y-x)$ = cc. due to carbonate,
and $y-2(y-x)$ or $2x-y$ = cc. due to hydroxide.

Analysis of Sodium or Potassium Carbonate and Bicarbonate. Dissolve a considerable amount of the sample in freshly boiled distilled water and make up to volume. Test a small portion for the presence of hydroxide by treating with $BaCl_2$ as previously described.

Total Alkali.—Pipette out an aliquot corresponding to 1 gram, or more if necessary, into a 500-cc. beaker. Add 3 drops of methyl orange and titrate rapidly to the end-point. This is merely a preliminary titration. Then take another aliquot and add 1 cc. less of 0.5 N acid than required by the first titration, taking care not to lose any liquid by effervescence. Cover the beaker with a watch glass, boil off the liberated CO_2, cool, add 2 drops of methyl orange and titrate to the exact end-point. In this titration, stir well when approaching the end-point and add the acid a drop at a time so that the color change will be sharp.

Caustic Alkali.—If the sample contains hydroxide, pipette an aliquot corresponding to 1 gram into a 250-cc. beaker and add 100 cc. of 10% $BaCl_2$ solution. Stir thoroughly, add 5 drops of phenolphthalein indicator and titrate cold with 0.5 N acid. Calculate the titration to NaOH or KOH.

Note.—If the sample contains hydroxide it cannot contain bicarbonate. In this case subtract the titration required by the hydroxide from the titration of total alkali and calculate the difference to carbonate.

Bicarbonate.—Pipette an aliquot corresponding to 5 grams into a 250-cc. beaker and titrate with 0.5 N NaOH solution until a drop of the solution added to a drop of $AgNO_3$ indicator (10% solution) on a spot plate gives a dark coloration at once. Calculate the titration to bicarbonate.

Calculation.—1 cc. 0.5 N caustic = 0.04200 gram $NaHCO_3$.
= 0.05005 gram $KHCO_3$.

Notes.—(1) To obtain the true carbonate, subtract the titration required by bicarbonate from the titration for total alkalinity (both on the basis of 1 gram) and calculate the difference to carbonate.

(2) Carbonates of sodium and potassium (soda ash and pearl ash) when freshly made should not contain more than traces of bicarbonate. On exposure, however, they absorb CO_2 and H_2O and should therefore be analyzed for bicarbonates if an accurate test is desired.

Impurities.—The impurities generally encountered in alkalies are chlorides, sulfates, and iron and alumina. These are determined in the usual way. Before precipitating the sulfate, the solution should be boiled after adding HCl, in order to remove excess CO_2. Iron is best determined colorimetrically.

AMMONIUM HYDROXIDE

General.—Aqua ammonia (U. S. P.) is a solution containing 10% by weight of NH_3. Stronger aqua ammonia (U. S. P.) contains 28% by weight of NH_3. The latter is about the strength of the conc. ammonium hydroxide of commerce. The crude ammonia liquor of the gas works contains generally between 1.25 and 2% of NH_3 and is generally concentrated to 15-17% for shipment.

As ammonia is very volatile, the sample should be analyzed as quickly as possible after receipt and kept tightly stoppered at all times.

Specific Gravity.—Determine the sp. gr. with a hydrometer or the Westphal balance at 15.5° C. For accurate work the temperature should be adjusted within a degree or so. For ordinary commercial purposes, however, the sp. gr. may be taken at room temperature and corrected to 15.5° C. by means of standard ammonia tables. As the coefficient varies with different temperatures, the correction cannot be made by formula.

Ammonia, NH_3. Refined Ammonia Water.—For strong liquors, pipette 25 cc. into a weighing bottle, stopper tightly and weigh. Then using the same pipette and allowing it to drain for the same length of time, pipette another 25 cc. into a 250-cc. volumetric flask two-thirds filled with water. Hold the tip of the pipette very near the surface of the water. Dilute to the mark with water and mix thoroughly. Titrate 25 cc. of this with 0.5 N HCl, using methyl red or methyl orange indicator (see p. 89, note 3). From the weight of sample taken and the titration, calculate the percentage of NH_3 by weight.

Calculation.—1 cc. of 0.5 N HCl = 0.008516 gram NH_3.
= 0.017524 gram NH_4OH.

NOTE.—The above proportions are for conc. ammonia water. For weaker samples correspondingly larger aliquots should be taken for analysis.

CRUDE AMMONIA LIQUOR.—Crude ammonia liquor from gas works contains ammonium sulfate and other salts as well as free NH_3, and in such samples the *total ammonia* should be determined.

For concentrated liquors, dilute 25 cc. to 250 cc. exactly as described under Refined Ammonia Water. Then pipette 25 cc. of this solution into a round-bottomed flask which can be connected to a condenser through a spray trap. This flask should contain about 100–150 cc. of distilled water. Add a few grains of granulated zinc or small pieces of pumice and about 5 grams of NaOH. Connect to the condenser and distill into 50 cc. of 0.5 N HCl, to which has been added a drop or two of methyl orange or methyl red (see p. 89). The lower end of the condenser should be connected to an adaptor which dips below the surface of the acid. Continue the distillation until about 100 cc. of liquid have come over. If the indicator in the 0.5 N acid should lose its pink color, add 25 cc. more of 0.5 N acid immediately. In such case, the distillation should also be repeated, distilling into a larger amount of acid to make sure that no NH_3 was lost. Titrate the excess of 0.5 N acid with 0.5 N or 0.1 N caustic and calculate the difference to NH_3, as previously described.

NOTE.—The above procedure is for concentrated liquors. For the *weak liquors* it is not necessary to make up to volume, but 25 or 50 cc. may be distilled directly after adding caustic. For the very weak *waste liquors*, at least 100 cc. of the sample should be taken for each distillation. The latter should show only a few hundredths of 1% of NH_3 when the concentrating still is running efficiently.

TABLE SALT

General.—The U. S. standard for table or dairy salt requires that it shall contain on the water-free basis not more than the following amounts of impurities:

1.4% Calcium Sulfate
0.5% Calcium and Magnesium Chlorides
0.1% Insoluble in Water*
0.05% Barium Chloride

* In December 1924 the U. S. Bureau of Chemistry modified the standard until further notice so that the Insoluble in Water is understood to mean material exclusive of insoluble $CaSO_4$.

In addition to these substances, table salt sometimes contains small amounts of calcium phosphate and sodium and magnesium sulfates. In shaker salt $MgCO_3$ is often added in amounts up to 1% to prevent caking. Natural salt also may contain small amounts of sodium carbonate, potassium chloride, and other impurities.

Express all results of analysis (except moisture) as percentages of the moisture-free material.

Appearance.—Examine the material under the microscope and note its general appearance. It should be homogenous and free from foreign matter. Add a drop of dil. HCl to the salt on the slide and note if there is any effervescence (CO_2).

Solubility and Reaction.—Make a nearly saturated solution with distilled water. Test with sensitive litmus paper. A turbidity which dissolves on the addition of acid indicates calcium phosphate or carbonate.

Preparation of Sample.—Pass the sample through a 20-mesh sieve, grinding if necessary. Avoid undue grinding, however, so that as much of the sample as possible will be retained on an 80-mesh sieve. Mix the sample by quartering and weigh all needed portions as nearly at the same time as possible.

Moisture.—Place about 10 grams of the sample in a dry, weighed Erlenmeyer flask of about 200-cc. capacity. Weigh the flask and sample. Spread the sample evenly over the bottom of the flask by shaking gently and insert a small funnel in the neck. Heat the flask and sample for periods of 1 hour each on a triangle over the low, open flame of a gas stove at a temperature of about 250° C. until two consecutive weighings agree within 0.005 gram. Shake the flask occasionally so that the sample will dry evenly. Report the loss in weight as Moisture.

Phosphoric Anhydride.—Dissolve 25 grams in distilled water. If the sample contains insoluble Ca salts, add just enough HNO_3 to clear up the turbidity. Filter, if necessary, dilute to 250 cc. in a volumetric flask, mix thoroughly, and pipette out 100 cc. (equivalent to 10 grams). Add 10 cc. of conc. HNO_3, then add NH_4OH until the acid is nearly but not completely neutralized. Add an excess of ammonium molybdate solution, warm gently and let stand 1 hour. If phosphate is present, a yellow precipitate will form. If the solution is colored bright yellow but does

not precipitate, report a trace of phosphate. Filter any appreciable precipitate and wash with 5% NH_4NO_3 solution. This precipitate may be filtered on a weighed filter paper, dried in a weighing bottle at 105° C. and weighed as ammonium phosphomolybdate. (In this case, of course, the final washings must be with cold water to remove the NH_4NO_3.)

CALCULATION.—$(NH_4)_2HPO_4 \cdot 12MoO_3 \times 0.038 = P_2O_5$.

For more accurate results, dissolve the precipitate in NH_4OH, add an excess of 5% H_2SO_4, run through a Jones reductor and titrate the Mo with 0.1 N $KMnO_4$.

CALCULATION.—1 cc. 0.1 N $KMnO_4 = 0.000203$ gram P_2O_5.

NOTE.—Both of the above methods for P_2O_5 are dependable only for the determination of small amounts.

Insoluble in Water.—Place 10 grams of the sample in a 250-cc. beaker. Add 200 cc. of water at room temperature and let stand 0.5 hour, stirring frequently. Filter through a weighed Gooch crucible with an asbestos mat previously dried at 110° C. Transfer the residue to the crucible with the aid of a rubber policeman, using a total of not more than 50 cc. of water. Wash the residue with small portions of water, about 10 portions of 10 cc. each, until 10 cc. of the filtrate shows only a faint opalescence upon addition of a few drops of $AgNO_3$ solution. Dry the crucible and contents to constant weight at 110° C. Report the residue as "matter insoluble in water." If it exceeds 0.1% determine its nature.

Sulfur Trioxide. *Preparation of Solution.*—Dissolve 20 grams of the sample in 150 cc. of water and 50 cc. of conc. HCl in a 400-cc. beaker. Cover the beaker, heat to boiling, and continue boiling gently for 10 minutes. Filter into a 500-cc. volumetric flask and wash the residue with small amounts of hot water until the filtrate is free from Cl. Unite the filtrate and washings, cool and dilute to volume. (Solution *A*.)

Determination.—Place 250 cc. of Solution *A* (equivalent to 10 grams) in a 400-cc. beaker, heat to boiling, and add a slight excess of a hot 10% $BaCl_2$ solution, drop by drop while stirring. Concentrate by heating gently and finally evaporate to dryness on the steam bath, stirring the partly dry residue toward the end. Wash the precipitate by decantation with small quantities

of hot water, finally transferring the precipitate to a close-grained filter paper with the aid of a rubber policeman and a stream of hot water. Wash the precipitate on the filter until the filtrate is free from Cl. Test the filtrate for the presence of SO_3. Dry, ignite, and weigh as $BaSO_4$. Calculate to SO_3.

CALCULATION.—$BaSO_4 \times 0.3430 = SO_3$.

Iron Oxide and Alumina. (*a*) *In the Absence of* P_2O_5.—To the remaining 250 cc. of solution *A* (equivalent to 10 grams) add a few drops of conc. HNO_3 and boil to oxidize Fe. Then add a slight excess of NH_4OH, boil until the odor has nearly disappeared, filter, wash with hot water, ignite in a blast lamp and weigh as $Fe_2O_3 + Al_2O_3$.

(*b*) *In the Presence of* P_2O_5.—To 250 cc. of solution *A* add slightly more than enough Fe_2O_3 to combine with the P_2O_5. (This should be calculated from the amount of P_2O_5 as determined on a separate sample.) To determine the correct amount of Fe to add proceed as follows:

Weigh out 1 gram of ferrous ammonium sulfate, dissolve in a little water, boil with a few drops of conc. HNO_3, make up to 100 cc. and use the proper aliquot as calculated from the following approximate factors:

$P_2O_5 \times 1.12 = Fe_2O_3$.

$Fe_2O_3 \times 5 =$ Ferrous ammonium sulfate.

Ferrous ammonium sulfate $\times 0.2036 = Fe_2O_3$.

After adding the iron solution, add a slight excess of NH_4OH and boil until the odor is nearly gone. This precipitates all the P_2O_5 as $FePO_4$ and the excess of Fe as $Fe(OH)_3$. Filter, wash, ignite, blast and weigh as $Fe_2O_3 + Al_2O_3 + P_2O_5$. From this weight subtract the amount of P_2O_5 previously determined and the weight of Fe_2O_3 added. The remainder will be the $Fe_2O_3 + Al_2O_3$ in the salt.

Total Lime.—To the filtrate from the NH_4OH precipitate add an excess of 10% oxalic acid solution (10 cc. usually are sufficient). Then add a few drops of methyl orange solution and neutralize while hot by adding conc. NH_4OH drop by drop, stirring constantly. Add about 1 cc. excess of the NH_4OH, stir, and let stand in a warm place for 3 hours. Decant the supernatant liquid through a filter, reserving the filtrate for the determination of MgO. Test the filtrate for CaO with $(NH_4)_2C_2O_4$ solution.

Wash the precipitate in the beaker once with 10 cc. of 1% $(NH_4)_2C_2O_4$ solution, decanting through the filter paper. Combine the filtrate and washings. Dissolve the precipitate in the beaker and on the filter with hot, dil. HCl, dilute to 100 cc., add a little $H_2C_2O_4$, and reprecipitate as before. After standing 3 hours, filter and wash with $(NH_4)_2C_2O_4$ solution as before, reserving the filtrate and washings. Transfer the precipitate to the filter, dry, ignite, and heat over a blast lamp to constant weight as CaO.

NOTE.—The CaC_2O_4 may also be titrated directly with 0.1 N $KMnO_4$ in the usual way (see p. 697).

Magnesia.—Combine the filtrates and washings from the CaO determination and concentrate if necessary, by boiling gently, to a volume of about 150 cc. Add about 2 grams of $(NH_4)_2HPO_4$ and sufficient HCl to clear the solution when the phosphate is all dissolved. Na_2HPO_4 or $NaNH_4HPO_4$ may be used instead of the $(NH_4)_2HPO_4$. When cold, make slightly alkaline with NH_4OH, stirring constantly. Add 1-2 cc. excess of NH_4OH and let stand about 12 hours. Filter off the supernatant liquid and wash three or four times by decantation with dil. NH_4OH (1:10). Dissolve the precipitate in HCl, dilute to about 75 cc., add a little $(NH_4)_2HPO_4$ and precipitate with NH_4OH as before. Let stand 6–12 hours, filter, wash free from Cl, ignite, blast, and weigh as $Mg_2P_2O_7$. Calculate to MgO.

CALCULATION.—$Mg_2P_2O_7 \times 0.3621 = MgO$.

Barium Chloride.—If SO_3 is found, Ba cannot be present in the solution but might be present in the insoluble. If SO_3 was not found, test for Ba by adding 5 cc. of dil. H_2SO_4 to 100 cc. of the solution prepared for the P_2O_5 determination (equivalent to 10 grams). Heat to boiling and let stand several hours, preferably over night. If there is a precipitate, filter the solution hot, wash with hot water, ignite in a platinum crucible and weigh as $BaSO_4$. Calculate to $BaCl_2$.

CALCULATION.—$BaSO_4 \times 0.8923 = BaCl_2$.

Potash.—The determination of K_2O is seldom necessary. If desired, proceed according to page 61.

Sodium Chloride.*—Dilute 25 cc. of the solution prepared for the P_2O_5 determination to 250 cc. Thoroughly mix and pipette out 50 cc. of this solution, equivalent to 0.5 gram of the sample.

* This is ordinarily calculated "by difference."

Dilute to about 250 cc., add 5 cc. of dil. HNO_3 and precipitate in a large Erlenmeyer flask, preferably glass-stoppered, with an excess of $AgNO_3$ solution. Shake violently, let stand in the dark until clear, at least 1 hour, filter on a weighed Gooch crucible, wash with water containing a few drops of $AgNO_3$ solution and finally wash once with boiling distilled water. Dry at 105° C., place the Gooch crucible in a large platinum crucible, and heat *gently* until the edges of the AgCl just *begin* to fuse. Cool in a desiccator and weigh. Calculate to NaCl.

CALCULATION.—$AgCl \times 0.4078 = NaCl$.

Calculations.—Calculate SO_3 to $CaSO_4$. If there is an excess of SO_3, calculate this to $MgSO_4$, and if still an excess, to Na_2SO_4. If CaO is in excess of SO_3, calculate the excess to $CaCO_3$ (if the salt solution is turbid and shows presence of carbonates) or to CaO (if the salt solution is alkaline) or to $CaCl_2$ (if the solution is clear and neutral).

All P_2O_5 must first be calculated to $Ca_3(PO_4)_2$, and any excess over CaO to $Mg_3(PO_4)_2$, and any further excess to Na_2HPO_4. Any excess of MgO over SO_3 or P_2O_5 calculate to $MgCO_3$, MgO or $MgCl_2$ (under the same conditions as for CaO). Report Fe_2O_3 and Al_2O_3 as such.

If any $BaCl_2$, $CaCl_2$ or $MgCl_2$ is present, subtract the equivalent amount of AgCl from the total AgCl before calculating the latter to NaCl.

If any potash is present, calculate it to KCl and subtract the equivalent amount from the NaCl.

NOTE.—If the amount of iron is desired, it is best determined colorimetrically, as in water analysis (see p. 691).

FACTORS.—$SO_3 \times 1.700 = CaSO_4$.
$SO_3 \times 1.504 = MgSO_4$.
$SO_3 \times 1.774 = Na_2SO_4$.

$CaO \times 1.785 = CaCO_3$.
$CaO \times 1.321 = Ca(OH)_2$.
$CaO \times 1.979 = CaCl_2$.

$P_2O_5 \times 2.184 = Ca_3(PO_4)_2$.
$P_2O_5 \times 1.852 = Mg_3(PO_4)_2$.
$P_2O_5 \times 2.000 = Na_2HPO_4$.

$MgO \times 2.092 = MgCO_3$.
$MgO \times 2.362 = MgCl_2$.

$CaCl_2 \times 2.583 = AgCl$.
$MgCl_2 \times 3.010 = AgCl$.
$BaCl_2 \times 1.376 = AgCl$.
$KCl \times 1.923 = AgCl$.

$K_2O \times 1.583 = KCl$.

REFERENCE.—Association of Official Agricultural Chemists: "Methods of Analysis," 112 (1925).

SODIUM NITRITE

Determination of $NaNO_2$.—Weigh out on a balanced watch glass exactly 4 grams of the sample and dissolve in water. Filter, if the solution contains much suspended matter. Dilute to 1 liter in a volumetric flask.

Into a clean Erlenmeyer flask of 300-400-cc. capacity pipette 50 cc. of 0.1 N $KMnO_4$ solution and dilute with 150 cc. of water. Pipette into this 25 cc. of the nitrite solution to be analyzed, equivalent to 0.1 gram of the original sample. Heat just to boiling. Add 20 cc. of dil. H_2SO_4 and let stand 10 minutes. Cool under the tap. Add 30 cc. of 10% KI solution. Upon adding the H_2SO_4 there will be a heavy precipitate of MnO_2, but the KI solution will dissolve this and should give a perfectly clear, brownish-red solution. Titrate this with 0.1 N thiosulfate, adding about 5 cc. of starch solution when the color begins to pale.

Run a blank with 50 cc. of the 0.1 N $KMnO_4$ solution, going through all the operations except the addition of the nitrite solution, and subtract from the blank the titration of the sample. Calculate the difference to $NaNO_2$.

CALCULATION.—1 cc. 0.1 N $Na_2S_2O_3 = 0.003450$ gram $NaNO_2$.

NOTE.—After adding the H_2SO_4 to the hot solution, the liquid should be distinctly pink or magenta after allowing the precipitate to settle. If it is not, too little $KMnO_4$ has been used, and the analysis must be repeated with a larger excess.

SODIUM SULFIDE

General.—Sodium sulfide occurs commercially in two forms—(1) crystals, $Na_2S \cdot 9H_2O$, containing theoretically 13.35% S; and

(2) fused sodium sulfide, Na_2S, containing theoretically 41.07% S. As a matter of fact, the crystals often contain more than the theoretical amount of S, due to loss of moisture; and the fused material is seldom completely dehydrated and usually contains about 25% S or 62% Na_2S.

Sulfide-sulfur.—Dissolve 10 grams of the material in water and make up to 500 cc. Pipette out 25 cc. and add to this 50 cc. of 0.1 N iodine (more if necessary). Titrate back the excess of iodine with 0.1 N thiosulfate. The iodine precipitates sulfur according to the reaction: $Na_2S+I_2=2NaI+S$.

Calculate the percentages of S and of Na_2S.

CALCULATIONS.—1 cc. 0.1 N iodine = 0.001603 gram S.
= 0.003903 gram Na_2S.

NOTE.—This determination is the only determination generally necessary. If it is desired to determine iron, dissolve 5 grams, acidify with HCl, boil off H_2S, add a few drops of HNO_3 and continue boiling. Filter, precipitate iron in the filtrate with NH_4OH, dissolve in hot 5% H_2SO_4, pass through a Jones reductor (see p. 186) and titrate with standard permanganate (or determine colorimetrically in the usual manner).

SODIUM SILICATE (WATER GLASS)

General.—Anhydrous water glass is generally given the formula $Na_2Si_4O_9$, containing 20.45% of Na_2O. According to the method of manufacture, however, its actual composition varies considerably from this and in commerce it is furnished as a thick solution, generally of a gravity either 40, 50, or 60° Bé. When exposed to the air, it sets first to a stiff jelly and then to a hard mass.

Specific Gravity.—If the solution is thin enough, determine the sp. gr. with a hydrometer. Otherwise fill a volumetric flask to the mark with the solution and compare its weight with an equal volume of water at the same temperature.

Moisture.—The moisture is not completely given off at 105° C. To get accurate results the material must be ignited.

Weigh accurately about 10 grams in a beaker. Dilute with water, transfer to a 500-cc. volumetric flask and make up to the mark. Mix thoroughly, pipette 50 cc. into a weighed platinum dish and evaporate on the steam bath. Dry in the oven at 105° C. and finally ignite cautiously to avoid spattering. Subtract the weight of residue from the weight of the aliquot taken and calculate the percentage loss on ignition. Report as Moisture.

Silica.—Place another aliquot of 50 cc. of the solution in a platinum dish, dilute to about 100 cc., add slowly 5 cc. of conc. HCl and evaporate to dryness. Heat at 135° C. for 2 hours, add a little conc. HCl and then 5 cc. of water. Warm a few moments, filter and wash with hot water. Evaporate the filtrate to dryness and heat as before for 0.5 hour. Take up with conc. HCl and water and filter. Combine both silica residues in a weighed platinum crucible, dry in the oven, then ignite intensely with a blast lamp, cool in desiccator, and weigh. Report the result as Total SiO_2.

NOTE.—From the above figure the amount of sodium silicate can be approximately calculated as follows: $SiO_2 \times 1.258 = Na_2Si_4O_9$.

Sodium Oxide.—The Na_2O *alkalinity* can be determined by titrating with 0.1 N acid and phenolphthalein. Take an aliquot of 50 cc., corresponding to 1 gram, dilute to 500 cc. with water free from CO_2 and titrate until the pink color of the phenolphthalein just disappears. Calculate to Na_2O.

CALCULATION.—1 cc. 0.1 N acid = 0.003100 gram Na_2O.

(2) The *total* Na_2O, which will include the sodium of impurities, such as sodium chloride and sulfate, is determined as follows:

Combine the filtrates from the SiO_2 determination, add a slight excess of NH_4OH, and boil. Then add a few cc. of ammonium carbonate solution and digest for some time. If any precipitate forms, filter it off. Make the filtrate slightly acid with H_2SO_4 and evaporate to dryness in a weighed platinum dish. Ignite until no more white fumes are given off. Saturate with water, add a few drops of ammonium carbonate solution, evaporate to dryness, again ignite and weigh as Na_2SO_4. Calculate the total Na_2O.

CALCULATION.—$Na_2SO_4 \times 0.4364 = Na_2O$.

Sodium Sulfate and Chloride.—If it is desired to determine these impurities, proceed in the usual way, using a very dilute solution. Make the solution acid in the cold, adding dil. acid a little at a time. If conc. acid or heat is applied, the silicic acid will precipitate. In determining sulfate, the solution may be heated after it has been made acid, if it is sufficiently dilute.

SODIUM HYPOCHLORITE BLEACH LIQUOR

General.—Sodium hypochlorite bleach liquor is usually made by one of the following processes:

(1) Electrolysis of a solution of common salt

(2) Action of Na_2CO_3 or Na_2SO_4 on bleaching powder (calcium hypochlorite) solution.

(3) Passing Cl gas into a solution of NaOH.

The first process does not make a strong hypochlorite solution; the second gives a solution containing about 5% of available Cl; the third process not only makes a strong solution containing 10–15% of available Cl, but the solution is more stable.

On account of the wide difference in strength of hypochlorite solutions the amount of sample to be taken for each determination cannot be definitely stated. In the following directions it is assumed that the solution contains about 10% of available Cl. If the liquid is much stronger than this, correspondingly less amounts should be taken, and in very weak solutions larger samples should be employed.

Specific Gravity.—Determine the sp. gr. at 60° F. with the Westphal balance or other convenient means.

Free Alkali.—Pipette 25 cc. of the sample into a liter volumetric flask containing about 500 cc. of water. Dilute to the mark and pipette 50 cc. of the diluted solution, after thoroughly mixing, into a 300-cc. Erlenmeyer flask. Add about 150 cc. of water and an excess of KI. Then run in exactly 20 cc. of 0.5 N HCl. Titrate with 0.1 N $Na_2S_2O_3$ solution until the yellow color of the liberated iodine is discharged. Add 10 drops of 0.1% solution of sodium alizarin sulfonate (1 gram dissolved in 1 liter of water.) Titrate the excess of HCl with 0.5 N NaOH solution. (If sodium alizarin sulfonate is not available, methyl orange may be used for this titration.) Calculate the total free alkali in terms of NaOH.

Calculation.—Convert the titrations to the basis of 0.1 N solutions. From the amount of standard HCl added (100 cc. of 0.1 N HCl, the equivalent of 20 cc. of 0.5 N HCl) subtract the number of cc. of 0.1 N $Na_2S_2O_3$ added and also subtract the back titration with 0.5 N NaOH solution, the latter multiplied by 5 to convert it to 0.1 N solution. The remainder is the amount of 0.1 N HCl required to neutralize the free alkalinity. From this calculate the percentage of free alkalinity in the sample in terms of NaOH.

1 cc. 0.1 N HCl = 0.00400 gram NaOH.

Reactions.—(1) $NaOCl+HCl=NaCl+HOCl$.
(2) $HOCl+2KI=KCl+KOH+I_2$.
(3) $I_2+2Na_2S_2O_3=2NaI+Na_2S_4O_6$.

Available Chlorine.—Add 50 cc. of 0.1 N arsenious acid solution to 50 cc. of the diluted solution of the original sample, mix well and titrate back the excess of As_2O_3 with 0.1 N iodine, adding a little starch indicator. From the amount of As_2O_3 consumed calculate the available Cl.

Calculation.—1 cc. 0.1 N $As_2O_3=0.003546$ gram Cl.

Sodium Hypochlorite.—NaOCl has an oxidizing value twice that of an equivalent quantity of chlorine water as shown by the following reaction:

$$2NaOCl+HC_2H_3O_2=2NaC_2H_3O_2+2HCl+O_2.$$

Consequently, calculate the percentage of NaOCl by multiplying the percentage of available Cl by the factor 1.050; or the amount of NaOCl may be calculated from the factor:

1 cc. 0.1 N $Na_2S_2O_3=0.003723$ gram NaOCl.

Total Chlorine.—Pipette 50 cc. of the diluted solution, into a 300-cc. Erlenmeyer flask. Add from a burette H_2O_2 in just sufficient quantity to destroy the available Cl, as indicated by starch-KI test paper. Boil out any excess of H_2O_2, make slightly acid with dil. HNO_3 and, after cooling, add an excess of $AgNO_3$ reagent. Let stand in a dark place until the AgCl settles clear. Filter on a weighed Gooch crucible, wash with hot water, suck the precipitate dry, then place the crucible in a large platinum crucible and heat with a low flame until the edges of the precipitate *just begin* to fuse. Cool in a desiccator and weigh as AgCl. Calculate to Cl.

Run a blank on the same amount of H_2O_2 as was used for the analysis and subtract any Cl found in it.

Calculation.—$AgCl\times0.2474=Cl$.

Note.—The total Cl thus determined does not include the Cl of any chlorate present. In samples containing chlorate the amount of Cl present as such should be added. ($NaClO_3\times0.3331=Cl$.)

Sodium Chloride.—This is calculated as follows: From the percentage of total Cl (exclusive of that due to chlorate) subtract one-half of the available Cl. Calculate the difference to NaCl.

Calculation.—$Cl\times1.6486=NaCl$.

Sodium Carbonate.—To 50 cc. of the diluted solution, heated to boiling, add an excess of $BaCl_2$ solution. Let stand, protected from CO_2 fumes, until the precipitate settles clear. Filter and wash with hot water free from CO_2. Ignite at a red heat in a weighed platinum crucible and weigh as $BaCO_3$. Calculate to Na_2CO_3.

CALCULATION.—$BaCO_3 \times 0.5370 = Na_2CO_3$.

NOTES.—(1) This method is not applicable if the material contains sulfates. In such cases, however, the ignited precipitate may be treated with warm dil. HCl to dissolve out the $BaCO_3$. The residual $BaSO_4$ may then be weighed and subtracted from the total precipitate to obtain the $BaCO_3$.

(2) The above method for carbonates tends to give slightly low results but is sufficiently accurate for most purposes.

Sodium Hydroxide.—From the free alkali, previously determined in terms of NaOH, subtract the amount of NaOH equivalent to the Na_2CO_3 above determined. The difference is NaOH alkalinity.

CALCULATION.—$Na_2CO_3 \times 0.7548 = NaOH$.

SODIUM BISULFITE

General.—Sodium bisulfite or bisulfite of soda, used for reducing purposes in the textile industries, generally occurs on the market in one of two forms: (1) Dry crystals of meta-bisulfite of soda ($Na_2S_2O_5$); or (2) so-called "Bisulfite liquor," which is usually a 33° Bé. solution containing 21% of SO_2 or 36.25% of $NaHSO_3$.

The only tests usually desired are the strength and, in case of the liquor, the density or specific gravity.

Specific Gravity.—Determine the sp. gr. at 15.5° C. with an accurate Westphal balance or hydrometer. Report both as specific gravity and as gravity Baumé.

Strength. META-BISULFITE CRYSTALS.—Pipette 100 cc. of 0.1 N iodine into a beaker. Weigh 0.4 gram of the sample into a small glass-stoppered weighing bottle. Immerse the stoppered end of the bottle in the iodine solution and withdraw the stopper slowly with a glass fork. Then stir the mixture until all the sample is dissolved. Titrate the excess of iodine with 0.1 N thiosulfate, adding a little starch indicator near the end. Calcu-

late the percentage strength of the sample from the amount of iodine consumed.

Calculation.—1 cc. 0.1 N iodine = 0.003203 gram SO_2.
= 0.004753 gram $Na_2S_2O_5$.

Bisulfite Liquor.—If the liquor is at 15.5° C., 10 cc. may be pipetted out and tested directly as described below. If, however, the temperature is not known, pipette 10 cc. into a weighing bottle, which has previously been weighed, and then weigh the bottle and contents. Fill a liter volumetric flask about three-fourths full of recently boiled and cooled water. Then, using the same pipette, at the same temperature, and allowing it to drain for the same length of time, pipette 10 cc. of the liquor into the water in this flask. Fill the flask to the mark with water and mix thoroughly.

Pipette into a beaker 50 cc. of 0.1 N iodine. Then pipette into this 25 cc. of the diluted solution of the sample. Titrate the excess of the iodine solution with 0.1 N thiosulfate from a burette, adding a little starch indicator towards the end. Multiply the number of cc. of iodine solution consumed by its proper factor, divide by one-fortieth of the weight of the original liquor taken and multiply by 100 to obtain the percentage of SO_2 or $NaHSO_3$.

Calculation.—1 cc. 0.1 N iodine = 0.003203 gram SO_2.
= 0.005203 gram $NaHSO_3$.

Note.—A table of the density of sodium bisulfite solutions and the corresponding percentage of $NaHSO_3$ and Baumé gravity is given in Van Nostrand's "Chemical Annual," 516, (1918).

Reference.—Knecht-Rawson-Loewenthal: "Manual of Dyeing", **2**, 784, (1910).

POTASSIUM OR SODIUM BICHROMATE

Potassium Bichromate.—Dissolve 8–9 grams of the sample, accurately weighed, in water and dilute to 1 liter. Pipette 25 cc. of this solution into a wide-mouthed, glass-stoppered bottle; add 15 cc. of a 10% KI solution and then 7 cc. of conc. HCl. Run in from a burette 0.1 N thiosulfate until the brown color is nearly gone. Then add a few drops of starch solution and complete the titration carefully until the color just changes from dark blue to light green.

Calculation.—1 cc. 0.1 N $Na_2S_2O_3$ = 0.004903 gram $K_2Cr_2O_7$.

Sodium Bichromate.—The same procedure may be used for the analysis of sodium bichromate, using the following factors for calculation:

1 cc. 0.1 N $Na_2S_2O_3$ = 0.004367 gram $Na_2Cr_2O_7$.
= 0.004967 gram $Na_2Cr_2O_7 \cdot 2H_2O$.

CYANIDES OF POTASSIUM AND SODIUM

General.—There is very little pure potassium cyanide on the market today. Most material so labeled contains varying amounts of sodium cyanide. As an insecticide or poison, however, it is chiefly bought and sold on the cyanogen content.

The following procedures are essentialy the official methods of the Association of Official Agricultural Chemists.

CAUTION.—Cyanides are extremely dangerous poisons. They should not be handled with the hands; and if necessary to grind them, a mask should be worn, to prevent inhaling the fine particles. On no account add a strong acid to a solution of a cyanide.

Cyanogen.—Weigh about 10 grams of the sample in a weighing bottle, dissolve in water, and make up to volume in a liter volumetric flask. Pipette a 100-cc. aliquot and titrate it with 0.1 N $AgNO_3$, drop by drop, stirring constantly, until 1 drop produces a permanent turbidity. In calculating the results, 1 equivalent of Ag is equal to 2 equivalents of CN, according to the equation: $2NaCN + AgNO_3 = NaCNAgCN + NaNO_3$.
Reserve the titrated solution for the determination of chlorine.

CALCULATIONS.—1 cc. 0.1 N $AgNO_3$ = 0.005202 gram CN.
= 0.009801 gram NaCN.
= 0.01302 gram KCN.

Chlorine.—After completion of the titration for cyanogen, as directed above, add a few cc. of 10% K_2CrO_4 solution as indicator and continue the titration with 0.1 N $AgNO_3$ to the appearance of the red-brown color of Ag_2CrO_4.

The first titration with $AgNO_3$ represents the CN present according to the above equation. The second titration represents the CN and Cl according to the following equation:.

$NaCNAgCN + NaCl + 2AgNO_3 = 2NaNO_3 + 2AgCN + AgCl$.

Therefore, subtract twice the first reading of the burette from the final reading and calculate the difference to chlorine or the chloride.

CALCULATION.—1 cc. 0.1 N $AgNO_3$ = 0.003546 gram Cl.
= 0.005845 gram NaCl.
= 0.007455 gram KCl.

REFERENCE.—Association of Official Agricultural Chemists: "Methods of Analysis," 65 (1925).

ACETATE OF LIME

General.—Commercial gray acetate of lime is the crude product from which acetic acid is obtained. In the distillation of wood, a

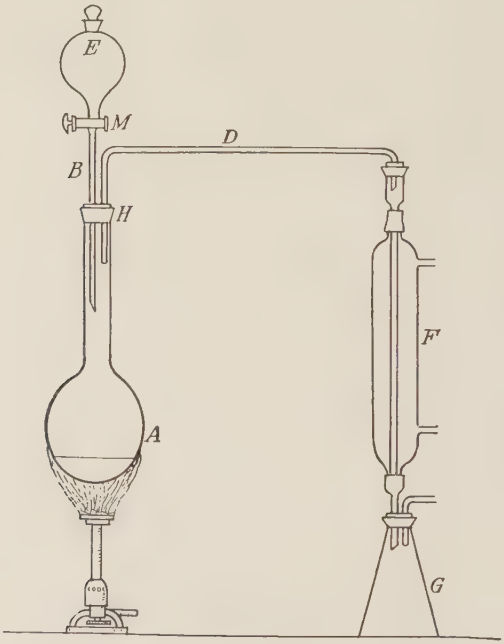

FIG. 2.—Apparatus for Analysis of Acetate of Lime.

mixture of acetic acid, wood alcohol, tar, etc., is obtained. The acetic acid and alcohol are separated by distillation from the tar. This mixture is neutralized with lime and the alcohol distilled off, leaving acetate of lime.

The only determinations which are usually necessary are the amounts of moisture and of true acetate of lime. A good grade of acetate should contain not more than 5% of moisture and should

show at least 80% of acetate of lime when analyzed by the following procedure:

Moisture.—Dry 5–10 grams at 100° C. for 2 hours. This is generally sufficient to drive off all the moisture, but to make certain of this, after cooling in a desiccator and weighing, return it to the oven for another half hour and again weigh. Report the total loss as moisture.

Acetate of Lime.—Determine the amount of acetic acid by distillation and calculate it to calcium acetate. The apparatus is shown in Fig. 2. Weigh accurately 2 grams of the sample into the long-necked, 250-cc. Kjeldahl flask *A*. Add 25 cc. of water and connect the flask by a 2-hole cork with the water reservoir (separatory funnel) *E* and the condenser *F*. Add to the flask 15 cc. of 85% H_3PO_4, sp. gr. 1.7. Boil the contents of flask *A* over a Rose burner until the contents are about 20 cc. The acetic acid and steam will be condensed and caught in the receiver *G*, to which has been added 30 cc. of 0.5 N NaOH solution.

Regulate the stop cock *M* so that the water will enter drop by drop into the flask *A*, keeping the contents at about 20 cc. Continue the distillation for 2 hours; remove the receiver *G*, replacing it with a fresh receiver, and titrate with 0.5 N NaOH and phenolphthalein. At the end of 15 minutes, titrate the amount of acid in the second receiver, if any. Continue the distillation until no more acetic acid comes over. From the total amount of 0.5 N NaOH neutralized, calculate the amounts of acetic acid and of calcium acetate.

CALCULATION.—1 cc. 0.5 N caustic = 0.03002 gram $HC_2H_3O_2$.
= 0.03954 gram $Ca(C_2H_3O_2)_2$.

NOTES.—(1) Make a careful blank with all reagents and correct for any acid obtained. This is very important and must not be neglected.

(2) It sometimes happens that at the end of 2 hour's distillation the liquid in the flask *G* is still alkaline. In such case titrate the excess alkalinity with 0.5 N HCl and subtract the titration. Continue the distillation, however, until a neutral distillate is obtained.

REFERENCE.—The above method was furnished by Stillwell and Gladding, New York, in 1909 and has given good results in this laboratory.

ANTIMONY SULFIDE

General.—The impure antimony pentasulphide used in the rubber trade is known as "Golden Sulfide of Antimony." It

can be made by boiling the crude black antimonious sulfide (Sb_2S_3) with hydrated lime, soda ash, charcoal and sulfur. The mixture is then filtered and concentrated to crystallization, giving Schlippe's salt, Na_3SbS_4. This, when treated with H_2SO_4, produces the orange pentasulfide, which is allowed to settle, washed by decantation and dried. It generally contains a considerable amount of calcium sulfate, free S, and antimony oxide (Sb_2O_3), but for rubber work should be entirely free from acids and chlorides. The free sulfur generally ranges from 5 to as much as 30%; the color varies from a full orange-tan to almost purple-scarlet. The behavior of different samples with boiling CS_2 varies widely; in some cases reduction to Sb_2S_3 takes place. The same is true of the behavior of different samples on drying at 110° C.

Free Sulfur.—Weight accurately 2 grams into a beaker and dissolve the Sb_2S_5 with conc. NH_4OH. Filter the residue on a filter paper, which has been dried and weighed in a weighing bottle, and wash with dilute NH_4OH until the filtrate shows no trace of Sb_2S_5 on acidulation with HCl. Dry this filter paper and contents for 5 hours (or to constant weight) at a temperature not over 60° C. The loss in weight is the Sb_2S_5, plus any moisture which may have been present. (For accurate work the moisture should be determined on a separate sample by drying at a temperature not above 60° C.)

Carefully fold the filter paper, place in an extraction thimble in a Soxhlet extractor, and extract for 12 hours with CS_2. Distill off most of the CS_2 into the top of the Soxhlet, *cool*, and remove the flask. Evaporate the rest of the CS_2 spontaneously, dry at not over 100° C. and weigh the free sulfur.

NOTES.—(1) Before disconnecting the flask it must be allowed to cool thoroughly, as hot CS_2 will ignite spontaneously.

(2) In case the determination of free S alone is desired and the analysis is urgent, it may be extracted directly with $CHCl_3$ or with acetone without the previous treatment with NH_4OH.

Antimony Oxide (Antimonious Acid).—Transfer the residue from the CS_2 extraction to a beaker. Evaporate off all CS_2 and then dissolve in 40 cc. of HCl. (If the material does not completely dissolve in HCl, add $\frac{1}{3}$ its volume of HNO_3 and evaporate to dryness. Then take up the residue with 40 cc. of conc. HCl.) To the HCl solution add 1 gram of potassium chlorate, boil until

all Cl is driven off and evaporate to about 25 cc. Cool and add enough water to dissolve any salts which may have crystallized. Add 1–2 grams of KI crystals and titrate with 0.1 N thiosulfate, using starch indicator. Do not add the starch until the titration is almost finished. Carry out the titration in an Erlenmeyer flask, preferably glass-stoppered, as otherwise iodine escapes when KI is added. The method depends upon the reduction of $SbCl_5$ to $SbCl_3$ by the KI and titration of the liberated iodine.

Calculation.—1 cc. 0.1 N thiosulfate = 0.00729 gram Sb_2O_3.
= 0.00609 gram Sb.

Calcium Sulfate.—If $CaSO_4$ is present, it is usually customary to confirm it qualitatively and report the amount "by difference," adding together the percentages of moisture, free S, Sb_2S_5 and Sb_2O_3 and subtracting from 100%.

References.—Weber, C. O.: "The Chemistry of India Rubber," 186; Heil and Esch: "Manufacture of Rubber Goods."

DETERMINATION OF SMALL AMOUNTS OF ARSENIC

General.—The three principal classes of materials (other than arsenic salts) in which arsenic often has to be determined are:

1. Foods, drugs, and chemicals.
2. Wall papers and textiles.
3. Arsenic bronzes.

The principal methods employed for the first two classes are the Marsh method and various modifications of the Gutzeit method. For the determination of arsenic in alloys see page 186.

Marsh Method

The apparatus consists of a generating flask (an ordinary 8-ounce wide-mouthed bottle with a 2-hole stopper is suitable) with a funnel tube, a U-tube containing cotton moistened with 10% lead acetate solution (to remove H_2S), a $CaCl_2$ drying tube, and a hard glass tube of 8-mm. bore drawn down near the end to a uniform constriction about 4 cm. long and 1 mm. inside diameter and also at the very end to a narrow exit tube. Instead of hard glass, transparent silica makes very satisfactory tubes. The tube is supported over a 3-burner furnace, the part in contact with the flame being wrapped with wire gauze.

Introduce into the generating flask 20–30 grams of arsenic-free zinc (either stick or mossy) and a perforated platinum disc to produce an electric couple. Insert the stopper and add through the funnel tube sufficient 20% H_2SO_4 to start the reaction and drive out all air. When any danger of explosion is over,* heat the tube to bright redness. After running the current long enough to prove the absence of As in the reagents, add slowly through the funnel tube a solution of the material in 20% H_2SO_4, or the solution obtained by one of the procedures described below, containing about 20% of H_2SO_4, keeping a steady evolution of gas. When the flow slackens, add 30% H_2SO_4 and later 40% H_2SO_4 until all the As has been expelled, which usually takes from 2 to 3 hours. If no As mirror forms in the constriction tube in 1 hour, further test may be abandoned.

If the amount of As is sufficient, cut off the constriction from the tube and weigh it, or weigh the whole tube. Then dissolve the As in a solution of sodium hypochlorite (Sb is insoluble). Wash with water and then with alcohol, dry, cool and weigh. The loss is metallic arsenic.

If the amount of As is very small, compare the mirror with a series of standard mirrors prepared in the same apparatus using quantities of a standard solution containing from 0.005 to 0.05 mg. of As_2O_3. To prepare the standard solution, dissolve 1 gram of pure As_2O_3 in arsenic-free NaOH solution. Acidify with H_2SO_4, make up to 1 liter and dilute 10 cc. of this stock solution to 1 liter. Of the latter solution 1 cc. = 0.01 mg. of As_2O_3.

Sanger-Black-Gutzeit Method (Modified)

Reagents.—(*a*) *Conc. Nitric and Sulfuric Acids, arsenic-free* (sp. gr. 1.42 and 1.84, respectively).

* Test for this as follows: Invert a small test-tube over the capillary exit of the Marsh tube, in a nearly vertical position, so that the test-tube will be gradually filled with the generated gas. Hold in this position for about 1 minute. Then place the thumb over the open end of the test-tube, reverse the position of the latter, bring the open end of the tube near a gas flame and remove the thumb. If the tube is filled with an explosive mixture, the contents will ignite with a peculiar noise resembling the yelp of a dog. Repeat this at intervals until the tube can be filled with a gas which is non-explosive and ignites quietly. As hydrogen is lighter than air the test-tube must be held inverted while filling and then reversed when brought to the flame.

(*b*) *Sulfuric Acid* (1:4), *or Hydrochloric Acid* (1:3), *both arsenic-free.*

(*c*) *Zinc, arsenic-free*—Stick zinc broken into pieces approximately 1 cm. in length.

(*d*) *Lead Acetate Paper*—Heavy filter paper soaked in 20% lead acetate solution, dried and cut into pieces about 4.5 by 16 cm.

(*e*) *Lead Acetate Cotton*—Absorbent cotton soaked in 5% lead acetate solution.

(*f*) *Mercuric Bromide Paper*—Cut heavy, close-textured drafting paper (similar to Whatman's cold pressed) into strips exactly 2.5 mm. wide and about 12 cm. long. Soak for an hour in a 5% solution of $HgBr_2$ in 95% alcohol, squeeze out the excess of solution and dry on glass rods. Cut off the ends of the strips before using.

(*g*) 20% *Potassium Iodide Solution.*

(*h*) *Stannous Chloride Solution*—40 grams of stannous chloride crystals made up to 100 cc. with conc. HCl.

(*i*) *Standard Arsenic Solution*—Dissolve 1 gram of As_2O_3 in 25 cc. of 20% NaOH solution, add about 475 cc. of recently boiled water, acidify with the dil. H_2SO_4 (1:4), add 10 cc. of conc. H_2SO_4 and dilute to 1 liter with recently boiled water. One cc. of this solution contains 1 mg. of As_2O_3.

Dilute 20 cc. of this solution to 1 liter. Fifty cc. of the latter solution when diluted to 1 liter give a dilute standard solution containing 0.001 mg. of As_2O_3 per cc., which is used to prepare the standard stains. The dilute solutions must be freshly prepared immediately before use.

Apparatus.—Use a 2-ounce wide-mouthed bottle as a generator. Fit this by means of a perforated rubber stopper with a glass tube, 1 cm. in diameter and 6 cm. long, containing a piece of the lead acetate paper rolled into a coil. Connect this tube by means of a perforated rubber stopper with a similar tube filled with the lead acetate cotton, squeezed to remove excess of the solution. The cotton in all tubes used should be uniformly moist to obtain comparative stains. Connect the second tube by means of a perforated rubber stopper with a narrow glass tube, 3 mm. internal diameter and 12 cm. long, containing a strip of the mercuric bromide paper (see Fig. 3). Rubber stoppers used for connections must be free from any white coating.

Preparation of Solution.—Weigh 5–50 grams of the finely divided and well-mixed sample into a porcelain casserole, the amount selected depending upon the character of the material and the ease with which it is oxidized. With dry, highly nitrogenous substances employ 5 grams; pulped vegetables, 25 grams; liquids with low solid content, like beer or vinegar, 50 grams. Add 10–15 cc. of the conc. HNO_3, cover the casserole by setting a watch glass inside the rim, convex side upward, heat until vigorous action is over, cool and add 10 cc. of the conc. H_2SO_4. Heat on a wire gauze over a flame until the mixture turns dark brown or black, then add more HNO_3 in 5-cc. portions, heating between each addition until the liquid remains colorless or yellow when evaporated until SO_3 fumes are evolved. To remove completely all nitric or nitrous acid, evaporate to about 5 cc., cool, dilute with 10–15 cc. of water and again evaporate until white SO_3 fumes are evolved. Cool, dilute with water, again cool, and make up with water to a definite volume (usually 25–100 cc., depending up on the amount of sample taken and its arsenic content).

FIG. 3. — Sanger-Black-Gutzeit Apparatus for Arsenic Determination.

Determination.—Introduce 20 cc. of the solution or, if the amount of arsenic is large, an aliquot containing about 0.03 mg. of As_2O_3 prepared as directed under Preparation of Solution, into the generator of the apparatus as described above and add 20 cc. of the dil. H_2SO_4 or of the dil. HCl. If the total volume is less than 40 cc., dilute to that volume with water, and add 4 cc. of 20% KI solution. Heat to about 90° C., add 3 drops of $SnCl_2$ solution and heat for 10 minutes. Cool the generator and its

contents to about 5° C. in a pan containing water and ice; when cold, add about 15 grams of the stick zinc and connect the entire apparatus as described above. Keep the bottles in ice water for 15 minutes, then remove from the bath and let the evolution of gas proceed for an hour longer. Remove the sensitized paper and compare the stain with similar ones produced under like conditions with known amounts of arsenic, using portions of the standard arsenic solution containing 0.001, 0.002, 0.005, 0.010, 0.015, 0.025 and 0.030 mg. of As_2O_3, adding such quantities of water and H_2SO_4 or HCl that the same volume and acid strength are maintained as in the determination.

NOTE.—It is very necessary in making comparisons that the same apparatus be used and the same proportions of the same reagents. Run a blank test on the reagents and correct for any arsenic found. The blank should not exceed 0.001 mg. of As_2O_3.

METHODS OF PREPARING SAMPLES FOR TEST

(1) Foods, Drugs, and Chemicals.

(*a*) *Syrups, baking powders, and other materials soluble in water or acid* do not need preliminary treatment.

(*b*) *Beer* is treated as follows: Measure 100 cc. (freed from CO_2 by agitation) in a 7-inch porcelain evaporating dish; add 20 cc. of pure conc. HNO_3 and 3 cc. of pure conc. H_2SO_4 and heat cautiously until vigorous chemical action sets in. Turn the flame low, or remove it altogether, and stir vigorously until the frothing ceases, after which the liquid may be boiled freely. Transfer to a large casserole and continue boiling until nearly all the HNO_3 is driven off. Then, holding the casserole by the handle, continue the heating until the mass chars and fumes of SO_3 are given off, giving the casserole a rotary motion to prevent spattering. The residue should be reduced to a dry, black, pulverulent char soon after the SO_3 fumes begin to come off freely. If still liquid, stir in pieces of filter paper while still heating until the residue is dry, avoiding an excess of paper. Cool, add 50 cc. of water and remove the masses of char from the sides of the dish with a stirring rod. Heat to boiling and filter Use the filtrate for the Marsh apparatus, adding it gradually.

(*c*) *Meat, vegetables, and the like* may be treated as follows, varying the proportion of acids to suit the conditions: Heat at 150–160° C. in a porcelain dish 100 grams of the finely divided material with 23 cc. of pure conc. HNO_3, stirring occasionally. When the mixture assumes a deep orange color, remove from the heat, add 3 cc. of pure conc. H_2SO_4 and stir while nitrous fumes are given off. Heat to 180° C. and add, while still hot, drop by drop with stirring, 8 cc. of HNO_3. Then heat at 200° C. until SO_3 fumes come off and a dry charred mass remains. Pulverize the mass, extract with hot water, filter, evaporate to small volume, take up in cold 20% H_2SO_4 and treat by the Marsh or Gutzeit method.

Alternative Method.—Digest at room temperature for some hours 5–20 grams of the material in a casserole with about an equal bulk of HNO_3. Add 20 cc. of conc. H_2SO_4 and digest further at a gentle heat until the mixture begins to char. Add about 2 cc. of HNO_3 and heat until SO_3 fumes appear, repeating the addition of acid and heating until oxidation appears to be practically complete. Remove all HNO_3 by dilution and evaporation to the fuming stage. Then dilute with 4 volumes of water. At this point about twice the bulk of saturated SO_2 solution may be added and the evaporation repeated, thus reducing to the arsenious condition, but this is not usually necessary.

(**2**) **Wall Paper and Textiles.**—Take a piece of paper 3.25×4 inches (equivalent to 0.01 sq. yd.) or a piece of cloth 12×10.8 inches (equivalent to 0.1 sq. yd.). Cut in small pieces and place in a porcelain dish or Kjeldahl flask. Add about 50 cc. of a mixture of 25 cc. conc. H_2SO_4 and 1 cc. conc. HNO_3, both As-free. Heat over a low flame until completely charred, and then continue heating until strong fumes of SO_3 appear. Cool, dilute, and filter into a liter volumetric flask. Cool, dilute to the mark and mix. Treat 250 cc. of this solution by the Gutzeit method, using 2 grams of arsenic-free zinc and letting the reaction run until the Zn is all dissolved. If a strong reaction is obtained, repeat, using a smaller aliquot. A very faint yellow color on the paper indicates the following amounts of metallic As per square yard:

Solution Taken cc.	Arsenic (Grains per Square Yard)	
	Paper	Cloth
500	0.007	0.0007
400	0.009	0.0009
300	0.012	0.0012
200	0.018	0.0018
100	0.036	0.0036
10	0.36	0.036
1	3.6	0.36

NOTES.—(1) The Massachusetts law allows not over 0.1 grain of metallic As per square yard of wall paper and not over 0.01 grain in dress goods.

(2) For court cases use the Marsh method and compare with standards.

REFERENCES.—Leach: "Food Inspection and Analysis," 1913 ed., 74 and 728; *J. Am. Chem. Soc.*, **11,** 250; *Proc. Am. Acad. Arts Sci.*, **26,** 24; *J. Soc. Chem. Ind.*, **26,** 1115 (1907); Association of Official Agricultural Chemists: "Methods of Analysis," 171 (1925).

DETERMINATION OF BORIC ACID

General.—The following methods have been adopted as official by the Associaton of Official Agricultural Chemists for the determination of borax or boric acid. For fertilizer materials and mixed fertilizers the Bartlett Method gives the water-soluble boron and is especially adapted to the analysis of samples relatively high in soluble phosphates or organic matter; the Ross-Deemer Method gives the acid-soluble boron and is preferable for samples low in soluble phosphates and organic matter relative to the B_2O_3 content. For the determination in foods see page 539.

Ross-Deemer Method.—REAGENTS REQUIRED.—(*a*) 10% *$BaCl_2$ Solution.*

(*b*) *Powdered $Ba(OH)_2$.*

(*c*) *Standard 0.1 N Boric Acid Solution.*

(*d*) *Standard NaOH Solution.*—Prepare this solution free from carbonates by first making a saturated solution of 100 grams in 100 cc. of water in order that any Na_2CO_3 present will be precipitated when the solution is allowed to stand in a vessel from which the CO_2 of the air is excluded. Filter through a hard filter that has been soaked in alcohol; dilute a portion to about 0.1 N with recently boiled and cooled water and accurately

determine the strength of the solution by titration against the standard boric acid solution as described below under the determination in mineral salts.

(*e*) *Two HCl Solutions*, one about 0.1 N and the other about 0.5 N.

(*f*) *Neutral Mannite* (*Mannitol*).

(*g*) *Methyl Red Solution.*—Dissolve 0.1 gram of methyl red in 50 cc. of 95% alcohol, dilute to 1 liter, and filter, if necessary.

(*h*) *Phenolphthalein Solution.*—Dissolve 1 gram in 100 cc. of alcohol.

DETERMINATION. *In Mineral Salts.*—Dissolve 5–10 grams of the sample in 50–75 cc. of hot water; decompose carbonates, if present, with a slight excess of conc. HCl; heat to boiling and add sufficient 10% $BaCl_2$ solution to precipitate the sulfates, using about 10 cc. in excess. Next add in small amounts sufficient powdered $Ba(OH)_2$ to make the solution alkaline, avoiding a large excess; boil for about 5 minutes, or until any NH_3 present has been expelled; filter and wash into a 300-cc. flask. Make acid with HCl, using an excess equivalent to a few cc. of 0.1 N solution. Boil for 15 minutes to expel CO_2, cool by placing the flask in cold water and bring to neutrality by first adding 4–5 drops of methyl red and then the standard NaOH solution until the color of the solution changes from pink to yellow. If the neutral point has been passed, or if there is any doubt as to this, restore the pink color by adding a few drops of approximately 0.1 N HCl and change the color to yellow again with the minimum amount of the standard NaOH solution. Add 1–2 grams of neutral mannite and a few tenths of a cc. of phenolphthalein solution; note the burette reading, and again titrate the solution with the standard NaOH solution until a pink color develops. Add a little more mannite and if the pink color disappears, continue the addition of the standard alkali until it again appears. Repeat until the addition of mannite has no further action on the end-point. If the content of H_3BO_3 in the solution titrated is low, one addition of mannite is usually sufficient. From the amount of the standard alkali required in the titration after the addition of mannite, corrected for the amount required when running a blank, calculate the quantity of borax or boric acid in the sample.

CALCULATION.—1 cc. 0.1 N NaOH = 0.006184 gram H_3BO_3.
= 0.005032 gram $Na_2B_4O_7$.
= 0.009536 gram $Na_2B_4O_7 \cdot 10H_2O$.

NOTE.—When an acid solution of the sample to be analyzed gives no precipitate upon the addition of a solution of $CaCl_2$ and sufficient NH_4OH to give an alkaline reaction, phosphates and Fe and Al salts are absent and that portion of the determination which involves treatment with $BaCl_2$ and $Ba(OH)_2$ for the removal of these constituents may be omitted.

In Mixed Fertilizers and Organic Compounds.—Weigh 5 grams of the sample into a 250-cc. beaker, add 50 cc. of hot water, cover with a watch glass, digest for 15–20 minutes on the water bath, filter and wash into another beaker of the same capacity. Heat the filtrate to boiling and add 15 cc. of 10% $BaCl_2$ solution, followed without undue loss of time by sufficient powdered $Ba(OH)_2$ to give an alkaline reaction with phenolphthalein. Boil for about 5 minutes, gently to prevent frothing over. Filter and wash, or, if preferred, make up to the mark in a volumetric flask and take an aliquot portion. Evaporate the filtrate or aliquot to dryness in a platinum or porcelain dish and ignite the residue, preferably in a muffle furnace at a temperature just below redness, until organic matter is completely carbonized. Treat the ignited residue with hot water, make slightly acid with HCl, heat nearly to boiling, make alkaline again with a slight excess of $Ba(OH)_2$ and filter into a 300-cc. flask. Acidify with dil. HCl (1:9), using an excess equivalent to a few cc. of a 0.1 N solution, boil to expel CO_2 and titrate as directed above under the determination in mineral salts.

NOTES.—(1) If the $Ba(OH)_2$ has been added only in slight excess, there is a tendency for the filtrate to become acid during evaporation with a possible loss of borax. It is therefore important that the solution be kept alkaline by repeated additions of $Ba(OH)_2$, if necessary, until the evaporation has been completed.

(2) If the filtrate from the $BaCl_2$-$Ba(OH)_2$ precipitate is titrated in this determination without first destroying soluble organic matter, the end-points in the titration will usually be too indefinite to give accurate results. The purpose in evaporating the filtrate and igniting the residue is therefore to get rid of soluble organic constituents which interfere with the titration. When the sample contains a relatively high H_3BO_3 content, in excess of 0.5%, a smaller sample may be taken and the quantity of organic matter

present may then be too small seriously to interfere with the sharpness of the end-points during the titration. When such is the case, boil the solution after the addition of the $Ba(OH)_2$ until any NH_3 present has been expelled. Omit evaporating the filtrate from the $BaCl_2$-$Ba(OH)_2$ precipitate. Add to the filtrate an excess of HCl equivalent to a few cc. of 0.1 N solution, boil to expel CO_2 and titrate as directed under the determination in mineral salts.

(3) In referring to borax in fertilizer materials the anhydrous $Na_2B_4O_7$ is meant, unless otherwise stipulated.

(4) For the determination of boric acid in foods, see page 539.

(5) For the determination of borax in soap, see page 373.

Bartlett Method.—Apparatus.—The apparatus consists of two 200-cc. round-bottomed flasks, a Liebig condenser and a 200-cc. Erlenmeyer receiving flask. One of the round-bottomed flasks *B* is supplied with a doubly perforated rubber stopper through which passes a glass tube running to the bottom of the flask. The other hole is supplied with a short tube leading to the condenser. The other round-bottomed flask *A* is fitted with a perforated rubber stopper and a short bent tube connected with a rubber tube to the long tube in flask *B*. The whole apparatus is supported by clamps and rings on two stands.*

Determination.—If the material is a mixed fertilizer or probably contains less than 2% of anhydrous borax, weigh 5 grams into flask *B*. If the sample is a chemical containing much more than 2% of borax, use 2 grams. Then add 5 cc. of 85% H_3PO_4 and 20 cc. of methyl alcohol and connect the flask with the condenser. Place 100 cc. of methyl alcohol in flask *A*. Set it in a water bath and connect with flask *B*. Place the receiving flask at the end of the condenser and apply sufficient heat to the water bath to keep a steady flow of bubbles of methyl alcohol passing through flask *B*. Some heat must also be applied to flask *B* to keep the volume at about 25 cc. When the lamps are once regulated they need very little attention and 2 distillations may easily be run at once.

Continue the distillation for about 30 minutes and distill 100 cc. When the distillation is complete add 2–3 drops of phenolphthalein indicator to the distillate and 5–10 cc. of 0.1 N NaOH, or sufficient to give a permanent pink. Stopper the flask, shake well and connect at once with a regular alcohol still supplied with

* See Leach: "Food Inspection and Analysis," 4th ed., 884 (1920).

a Hopkins' or similar bulb, distill off the alcohol and save for another determination. A water bath and not a direct flame should be used for this purpose.

Transfer the residue, which should be not less than 10 cc., to a platinum or porcelain dish, using as little water as possible, and evaporate to dryness on a steam or water bath. When dry, ignite below redness, then acidify with a few drops of normal HCl, add 20–25 cc. of water and warm for 1–2 minutes on the steam bath. Filter into a small flask, wash thoroughly and dilute to about 50–75 cc. Attach to an air-cooled condenser and boil slowly for a few minutes to remove CO_2. Add 3–4 drops of methyl red and then 0.1 N NaOH until the red color just disappears. Then add about 1 gram of mannite, or less if only a small amount of B_2O_3 is present. At this point if B_2O_3 is present, the solution will take on a pinkish color, the depth of color depending upon the amount present. Usually 0.01 or 0.02% is sufficient to give the reaction if the solution has been carefully neutralized with the NaOH. Then add 2-3 drops of phenolphthalein and titrate with 0.1 N NaOH which has been standardized against recrystallized boric acid. A blank should be run with the reagents but if the NaOH is free from CO_2, the blank should not be more than 0.2 cc. Calculate as under the Ross-Deemer Method above.

Reference.—Association of Official Agricultural Chemists: "Methods of Analysis," 16 (1925).

POTASSIUM IN FERTILIZERS, SOILS, PLANT ASHES, ETC., AND IN POTASH SALTS

(A) Lindo-Gladding Method

(1) **Reagents.**—(*a*) *Ammonium Chloride Solution.*—Dissolve 100 grams of NH_4Cl in 500 cc. of water, add 5 to 10 grams of pulverized K_2PtCl_6, and shake at intervals for 6–8 hours. Let the mixture settle overnight and filter. The residue may be used for the preparation of a fresh supply.

(*b*) *Platinum Solution.*—The platinum chloride solution used contains 1 gram of metallic platinum (2.1 grams of H_2PtCl_6) per 10 cc. For materials containing less than 15% of K_2O it is preferable to use this solution diluted 1:4.

(*c*) *80% Alcohol.*—Sp. gr. 0.8645 at 15° C.*

(2) Preparation of Solution.

(*a*) *Mixed Fertilizers.*—Place 2.5 grams of the sample upon a 12.5 cm. filter paper and wash with successive small portions of boiling water into a 250-cc. volumetric flask till the filtrate is about 200 cc. Add to the hot solution a slight excess of conc. NH_4OH and sufficient saturated $(NH_4)_2C_2O_4$ solution to precipitate all the lime present. Cool, dilute to 250 cc., mix, and pass through a dry filter.

(*b*) *Potash Salts; Muriate and Sulfate of Potash, Sulfate of Potash and Magnesia, and Kainit.*—Dissolve 2.5 grams and dilute to 250 cc. without the addition of NH_4OH and $(NH_4)_2C_2O_4$.

(*c*) *Organic Compounds.*—When it is desired to determine the total amount of K_2O in organic substances, such as cottonseed meal, tobacco stems, etc., saturate 10 grams with conc. H_2SO_4 and ignite in a muffle at a low red heat to destroy organic matter. Add a little conc. HCl, warm slightly in order to loosen the mass from the dish, transfer to a 500-cc. volumetric flask and proceed as directed above for Mixed Fertilizers (*a*).

(*d*) *Ashes from Wood, Cotton Hulls, etc.*—Boil 10 grams with 300 cc. of water for 30 minutes, add while hot a slight excess of conc. NH_4OH and then enough saturated $(NH_4)_2C_2O_4$ solution to precipitate all the lime present. Cool, dilute to 500 cc., mix and pass through a dry filter.

(3) Determination.

(*a*) *Mixed Fertilizers.*—Evaporate 50 cc. of the solution made according to (**2,** *a*), corresponding to 0.5 gram of the sample, nearly to dryness, add 1 cc. of dil. H_2SO_4 (1:1), evaporate to dryness, and ignite to perfect whiteness. All K_2O is in the form of non-volatile K_2SO_4 and a full red heat must be maintained until the residue is perfectly white. Dissolve the residue in hot water, using at least 20 cc. for each 0.1 gram of K_2O. Add a few drops of HCl and an excess of the platinum solution. Evaporate on a water bath to a thick paste in a porcelain dish and treat the residue with 80% alcohol, *avoiding exposure to* NH_3. Filter and wash the precipitate thoroughly with 80% alcohol both by

* Denatured alcohol, made up according to formula 30 (U. S. I. R. Reg. No. 30, revised) and diluted with water to make 80% by volume may also be used.

decantation and on the filter, continuing the washing after the filtrate is colorless. Wash finally five or six times with 10 cc. of NH_4Cl solution (**1,** *a*) to remove impurities from the precipitate. Wash again thoroughly with 80% alcohol and dry the precipitate for 30 minutes at 100° C. Weigh as K_2PtCl_6 and calculate to K_2O.

NOTE.—*The precipitate should be completely soluble in water.*

(*b*) *Muriate of Potash.*—Acidify 50 cc. of the solution prepared according to (**2,** *b*) with a few drops of HCl, add 10 cc. of Pt solution and evaporate to a thick paste. Treat the residue as under (**3,** *a*).

(*c*) *Sulfate of Potash, Sulfate of Potash and Magnesia, and Kainit.*—Acidify 50 cc. of the solution, prepared according to (**2,** *b*) with a few drops of conc. HCl and add 15 cc. of Pt solution. Evaporate the mixture and proceed as directed under (**3,** *a*), except that 25-cc. portions of NH_4Cl solution should be used.

(*d*) *Water-soluble Potash in Wood, and Cotton Hull Ashes, etc.*—Use method (**3,** *a*) above, making the solution according to (**2,** *a*), and pay special attention to the note.

(**4**) **Factors.**—For the conversion of K_2PtCl_6 to KCl, use the factor 0.3067; to K_2SO_4, 0.3584; and to K_2O, 0.1937.

(B) Optional Method

NOTE.—Method (A) is preferable in the presence of soluble sulfates.

Reagents.—The same as for the Lindo-Gladding method (A).

Preparation of Solution.—Prepare the solution as directed under the Lindo-Gladding method (A, 2) omitting in all cases the addition of ammonium hydroxide and oxalate.

Determination.—Dilute 25 cc. of the solution (50 cc. if less than 10% of K_2O is present) to 150 cc. Heat to boiling and add, drop by drop, and with constant stirring, a slight excess of 10% $BaCl_2$ solution. Without filtering, add in the same manner saturated $Ba(OH)_2$ solution in slight excess. Filter while hot and wash until the precipitate is free from Cl. Add to the filtrate 1 cc. of conc. NH_4OH and then a saturated solution of ammonium carbonate until the excess of Ba is precipitated. Heat and add, in fine powder, 0.5 gram of pure oxalic acid or 0.75 gram of $(NH_4)_2$-

C_2O_4. Filter, wash free from Cl, evaporate the filtrate to dryness in a platinum dish and ignite carefully over the free flame *below red heat* until all volatile matter is driven off. Digest the residue with hot water, filter through a small filter and dilute the filtrate, if necessary, so that for each 0.1 gram of K_2O there will be at least 20 cc. of liquid. Acidify with a few drops of HCl and add platinum solution in excess. Evaporate in a porcelain dish on the water bath to a thick paste and treat the residue repeatedly with 80% alcohol, both by decantation and after collecting on a weighed Gooch crucible. Dry for 30 minutes at 100° C. and weigh. If there is an appearance of foreign matter in the precipitate, wash as described above under Method (A) with several portions of 10 cc. each of the NH_4Cl solution.

Reference.—The above are the official methods of the Association of Official Agricultural Chemists: "Methods of Analysis," 2nd ed., 13 (1925).

POTASSIUM AND SODIUM IN ROCKS AND SILICIOUS MATERIALS

J. Lawrence Smith Method

Mix 0.5 gram of the sample, finely ground, with 0.5 gram of pure dry NH_4Cl, by gentle trituration in an agate mortar, then add 4 grams of dry powdered $CaCO_3$ and mix intimately.* Transfer the mixture to a large platinum crucible, rinsing the mortar with a little of the $CaCO_3$ powder. Place the crucible in a hole cut in a sheet of asbestos, the hole of such a size that not more than two-thirds of the crucible will be below the asbestos. Heat gently over a small Bunsen burner until fumes of NH_4 salts no longer appear. Then heat with a higher flame until the lower part of the crucible is brought to a red heat. Not more than three-quarters of the crucible should be red and it should be kept well covered during the fusion. Keep this temperature constant for 40–60 minutes.

The temperature desired is that which suffices to keep in a state of fusion the $CaCl_2$ formed by the reaction of NH_4Cl with $CaCO_3$. The mass, however, does not become liquid, since the fused $CaCl_2$ is absorbed by the large quantity of $CaCO_3$ present. The silicate itself should not fuse, since this would render impossible the disintegration of the mass at the end of the operation.

* For soils double the above amounts.

Moreover, too high a temperature causes a volatilization of alkali chlorides. Certain silicates, *e.g.*, those which contain much ferrous iron, may fuse when heated with the above mixture, even if no higher temperature is employed than is necessary to effect decomposition. If this occurs, it is better to repeat the ignition with a new portion, using 8–10 parts of $CaCO_3$.

The mass contracts in volume during the ignition, and is usually easily detached from the crucible. Boil it for 0.5 hour in a covered porcelain dish with 50–75 cc. of water, replacing water lost by evaporation. Decant the solution from the residue upon a filter, boil the residue a few minutes with water, and decant again. If the residue is now all in a finely disintegrated state, it may be brought upon the filter and washed. But if, as is often the case, a portion remains coherent or in a coarsely granular state, it must be reduced to a fine state of division by trituration with a porcelain or agate pestle in the dish, and boiling with water again. By a few repetitions of the trituration, boiling and decanting, allowing the fine suspended portion to pass upon the filter each time, the whole can usually be transferred to the filter in properly disintegrated condition in the course of an hour.

Next wash until a few drops of the washings acidified with HNO_3 give but a slight turbidity with $AgNO_3$.* The filtrate now contains the alkalies of the silicate as chlorides together with calcium chloride and hydroxide. It is not advisable to concentrate this filtrate in glass, since it might dissolve an appreciable quantity of sodium. Precipitate, therefore, the Ca at once with ammonium carbonate; let the precipitate settle, and concentrate the supernatant solution in a porcelain (or platinum) dish, decanting it into the latter, portionwise if necessary, finally rinsing the precipitate into the dish. When the volume is thus reduced to about 30 cc., add a little more ammonium carbonate and conc. NH_4OH, heat and filter into a platinum (or porcelain) dish. Evaporate to dryness on a water bath, expel NH_4Cl by gentle ignition, and dissolve the residual alkali chlorides in 3–5 cc. of water. A little black or dark-brown flocculent matter usually

* The residue should dissolve completely in dil. HCl without showing the least trace of undecomposed mineral, not even quartz, although sometimes a few black particles of iron ores will dissolve very slowly. If the residue is not completely soluble, the entire operation should be repeated.

remains undissolved, and the solution may still contain traces of Ca.

If potash alone is to be determined, proceed from this point as directed under (**3,** *a*) on page 62, beginning with "Dissolve the residue in hot water." Report as percentage of K_2O.

If both potash and soda are to be determined, after dissolving the alkali chlorides in 3–5 cc. of water add 2 or 3 drops of ammonium carbonate and conc. NH_4OH, warm gently, and filter through a very small filter into an unweighed but weighable platinum dish. Evaporate to dryness on a water bath, heat cautiously at dull red to incipient fusion and, after cooling, weigh. Dissolve the mixed chlorides in water and filter through a small filter into a porcelain dish. Ignite the filter in the platinum vessel previously used and weigh. Subtract this weight from the first weight to obtain the weight of the NaCl+KCl. Determine the K_2O in the filtrate in the porcelain dish. Add sufficient platinum chloride solution to combine with the total weight of alkali chlorides calculated as NaCl, *i.e.*, an amount of metallic Pt 1.67 times the weight of alkali chlorides found, and evaporate to a sirupy consistency. Add 15 cc. of 2.25 N acidulated alcohol (prepared by passing HCl gas into a mixture of 1000 cc. of 95% alcohol and 71 cc. of conc. HCl). Filter through a small filter, wash free from Pt salts with 80% alcohol, then with NH_4Cl solution (**1,** *a* on p. 61) and finally with 80% alcohol. Dry the precipitate on the filter, dissolve and wash through the filter with hot water into a weighed platinum dish, using suction. Evaporate to dryness, heat in the oven for an hour at 120° C., cool in a desiccator and weigh as K_2PtCl_6. Calculate to K_2O and to KCl. Deduct the KCl from the weight of combined NaCl and KCl to obtain the NaCl. Calculate the latter to Na_2O and express as percentage of the sample taken.

CALCULATIONS.—$K_2PtCl_6 \times 0.1937 = K_2O$.

$K_2PtCl_6 \times 0.3067 = KCl$.

$NaCl \times 0.5303 = Na_2O$.

NOTE.—Smith's method is the most convenient of all methods for extracting alkalies from silicates, and is universally applicable, except perhaps in the presence of boric acid. When carried out as here described, results are sufficiently accurate in most cases. If, however, the silicate is rich in alkalies, a loss amounting to 0.1 or 0.2% of the mineral is possible. If great

accuracy is desired in such cases, a repetition of the whole process may be applied to the residue left by treatment of the ignited mass with water. It need hardly be mentioned that unless care be taken to use reagents perfectly free from soda and to avoid action of the solution on glass, an amount of soda may be introduced from these sources equal to 0.1 or 0.2%.

REFERENCES.—Association of Official Agricultural Chemists: "Methods of Analysis," 2nd ed., 32 (1925); Fresenius: "Quantitative Chemical Analysis," 426.

LEAD ARSENATE

General.—Lead arsenate, furnished on the market as an insecticide, generally consists either of $Pb_3(AsO_4)_2$ or $PbHAsO_4$ or a mixture of the two. The former is prepared from lead acetate and sodium arsenate according to the reaction:

$$3Pb(C_2H_3O_2)_2 \cdot 3H_2O + 2Na_2HAsO_4 \cdot 7H_2O = Pb_3(AsO_4)_2 + 4NaC_2H_3O_2 \cdot 3H_2O + 2HC_2H_3O_2 + 11H_2O.$$

The second form is made from lead nitrate and sodium arsenate, probably according to the reaction:

$$Pb(NO_3)_2 + Na_2HAsO_4 \cdot 7H_2O = PbHAsO_4 + 2NaNO_3 + 7H_2O.$$

$Pb_3(AsO_4)_2$ contains theoretically 74.44% of PbO and 25.56% of As_2O_5. On the other hand, $PbHAsO_4$ contains theoretically 64.29% of PbO, 33.11% of As_2O_5 and 2.60% of water of constitution. In technical analysis it is often customary to report the sum of the total $PbO + As_2O_5$ as "Lead Arsenate." To give the seller full benefit, however, this sum should be divided by 0.9740 and the result reported as lead arsenate, thus allowing for the maximum amount of water of constitution.

Total Volatile Matter (Moisture, etc).—In case the sample is in the form of a paste, as it usually is, it should be very thoroughly and rapidly mixed, about 50 grams dried to constant weight in a flat glass Petri dish at 105° C. and the total loss in weight determined. Save a portion of the original paste for determination of free acetic acid and free ammonia, if these determinations are desired.

Grind the dried sample to a fine powder. Mix well, transfer a small portion to a sample bottle and again dry for 1–2 hours at 105–110° C. Use this anhydrous material for the determination of total PbO and total As_2O_5.

If the sample is a dry powder, dry 2 grams to constant weight at 105° C. and report the loss in weight as moisture.

Total Lead Oxide.—Dissolve 2.5 grams of the dry powder in 75 cc. of dil. HNO_3 (1:4) on the steam bath. The sample should dissolve without residue. (In case there is an appreciable residue, it may be filtered out, ignited and weighed and reported as Insoluble Matter.)

Transfer to a 250-cc. volumetric flask, cool to room temperature and make up to the mark. Pipette 50 cc. of this solution into a 600-cc. beaker; dilute to at least 400 cc.; heat nearly to boiling; add NH_4OH to incipient precipitation and then dilute HNO_3 (1:10) to redissolve the precipitate, avoiding more than 1–2 cc. excess. Add slowly from a pipette 50 cc. of a hot 10% solution of $K_2Cr_2O_7$, stirring constantly. Boil for 2 or 3 minutes. The $PbCrO_4$ will settle out, leaving a clear solution, in about 15 minutes.

Filter while still hot on a weighed Gooch crucible, washing thoroughly by decantation with hot water. Dry to constant weight at 140–150° C. and calculate to PbO.

Calculation.—$PbCrO_4 \times 0.6906 = PbO$.

Notes.—(1) The $PbCrO_4$ may contain a small amount of lead arsenate which causes slightly high results. This error rarely amounts to more than 0.1–0.2%.

(2) Instead of drying the $PbCrO_4$ at 140–150° C. it is permissible to dry at 105° C., then place the Gooch in a larger platinum crucible and ignite at dull redness. The flame must not come in direct contact with the $PbCrO_4$.

Total Arsenic.—Transfer 100 cc. of the HNO_3 solution prepared above to a porcelain or platinum dish, add 6 cc. of conc. H_2SO_4, evaporate to a syrupy consistency on the water bath and then on the hot plate to copious *white* fumes. Cool, add a little water and again evaporate to white fumes to insure removal of the last traces of HNO_3. Again cool, wash into a 100-cc. volumetric flask with water, and make up to the mark. Filter through a dry filter and use a 50-cc. aliquot for analysis. Transfer this to a 400-cc. Erlenmeyer flask, add 50 cc. of water and 1 gram of KI crystals. Boil until the solution is colorless or only faint yellow. The volume must not be allowed to become less than 50 cc. Cool the solution under running water, dilute to about 200 cc. and add a drop or two of 0.1 N $Na_2S_2O_3$ until the iodine color is just discharged; then add a drop of methyl orange indi-

cator and powdered Na_2CO_3, cautiously at first to avoid loss by foaming. When the solution, after mixing, becomes yellow, add just enough dil. H_2SO_4 to produce a pink color; and then make alkaline again with an excess of $NaHCO_3$ powder. Add 4 or 5 grams excess of bicarbonate. Titrate the solution with 0.05 N or 0.1 N iodine solution until the yellow color disappears slowly from the solution, add 5 cc. of starch indicator solution and continue the titration to the appearance of a blue color throughout the solution. Make a correction for the quantity of standard iodine solution necessary to produce the same color in a blank, using the same reagents and volume. From the amount of iodine used calculate the percentage of As_2O_5.

CALCULATION.—1 cc. 0.1 N iodine = 0.005748 gram As_2O_5.

NOTES.—(1) A generous excess of bicarbonate insures a sharp end-point in titrating.

(2) This method is not applicable in the presence of antimony. If Sb is suspected, use the method for Paris Green on page 76.

Lead Arsenate.—Add together the total PbO and As_2O_5; divide the sum by 0.9740 and report the result as Lead Arsenate.

Total Water-soluble Matter.—Weigh to 0.01 gram 4 grams of paste (or 2 grams if the sample is a dry powder), place in a tightly stoppered flask or bottle with 1 liter of freshly boiled and cooled distilled water and keep at 32° C. for 24 hours, shaking well every hour of the working day (eight times in all), filtering at the end of 24 hours. It is generally most satisfactory to filter through a Gooch crucible, rinsing out the filtering flask once or twice with the first portions of filtrate and discarding them. Continue the filtration until about 350 cc. of filtrate have been obtained. Fill with this a 250-cc. volumetric flask, first rinsing the latter several times with small portions of the liquid. Evaporate the entire 250 cc. in a weighed platinum dish to dryness on the steam bath. Dry to constant weight at 100° C. and weigh the total soluble matter. The weight in centigrams gives the direct percentage on a 4-gram sample.

NOTE.—In most cases it is sufficiently accurate to let stand for 2 or 3 days at room temperature (shaking frequently), instead of 24 hours at 32° C. The individual for whom the analysis is made often specifies the time for digesting for water-soluble impurities.

Water-soluble PbO.—Dissolve the residue of total soluble matter, above determined, in a small amount of water, add a few cc. of conc. HNO_3 and evaporate nearly to dryness on the steam bath; wash this into a small beaker with a little water, add 1 cc. of conc. H_2SO_4, evaporate to a syrup on the steam bath and then to white fumes on the hot plate. *Cool,* add 10 cc. of water, and swirl the beaker gently to throw any $PbSO_4$ into the center. If any is present, let stand 1 hour, or for very accurate work, overnight. Then filter on a tiny filter, and wash with 5% H_2SO_4 solution. Dry the filter paper and ignite in a weighed *porcelain* crucible. Treat the residue with a little HNO_3, which is afterwards evaporated off, and then with a drop or two of H_2SO_4. Ignite gently, cool and weigh as $PbSO_4$. Calculate to PbO.

CALCULATION.—$PbSO_4 \times 0.7360 = PbO$.

Water-soluble As_2O_5.—Water-soluble As_2O_5 is determined in the filtrate from the water-soluble PbO in exactly the same manner as for total As_2O_5 above, using, however, 0.01 N instead of 0.1 N iodine for titration. It is important that the solution shall be perfectly clear and the titration carefully made. Make corrections for the iodine necessary to produce the same color using the same chemicals and volumes of solution. (See note 2 at end of method.)

Free Acetic Acid.—Weigh out 2–10 grams of the original moist sample and transfer to a 250-cc. flask with 20–40 cc. of water. Connect with a condenser and heat to boiling. Pass steam through the solution, regulating the flame under the flask so that the volume will remain nearly constant, and collect about 200 cc. of distillate. Titrate the distillate with 0.1 N NaOH and phenolphthalein, and calculate to acetic acid.

CALCULATION.—1 cc. 0.1 N NaOH = 0.0060 gram $HC_2H_3O_2$.

Free Ammonia.—Wash 2–10 grams of the original sample into a 200-cc. distilling flask and dilute to about 150 cc. Concentrate by distillation to about 25 cc. and collect the distillate in a known volume of 0.1 N HCl. Titrate the excess of HCl with standard alkali, using methyl red or cochineal indicator, and calculate the NH_3 from the amount of acid consumed.

CALCULATION.—1 cc. 0.1 N HCl = 0.0017 gram NH_3.

Calculation of Results.—From the total loss on drying subtract any free acetic acid or free NH_3 which the sample may

contain, and report the difference as Moisture. In case free acetic acid and free NH_3 are not determined, it is customary to report the total loss on drying as Moisture, loss at 105° C.

Calculate the percentages of total PbO, total As_2O_5, and water-soluble impurities to the absolute dry basis. Then calculate these results to the original paste by multiplying each by 100% minus the percentage of total moisture at 105° C. Subtract the percentage of soluble As_2O_5 and of soluble PbO from the total soluble matter and report the difference as "Soluble Impurities."

NOTES.—(1) The procedures for Moisture, Total PbO, Total As, and Water-soluble As_2O_5 are essentially the methods of the Association of Official Agricultural Chemists as published in its "Methods of Analysis," 56 (1925), slight changes being made for convenience in conforming to our usage.

(2) Lead arsenate as now made seldom contains an appreciable amount of water-soluble PbO, consequently the water-soluble As_2O_5 can be determined directly on the filtered solution without going through the steps of removing lead.

BORDEAUX MIXTURE

General.—Standard Bordeaux Mixture is made up in the proportions of 6 pounds of $CuSO_4$ and 4 pounds of lime to 50 gallons of water; but a more common mixture is 5 : 5 : 50, and for peach trees the general mixture is 3 : 9 : 50.

The following procedures are essentially the official methods of the Association of Official Agricultural Chemists.

NOTE.—Bordeaux Mixture is often mixed with other insecticides. For analysis of such mixtures see page 74.

Moisture. *Powder.*—Dry 2 grams to constant weight at 105–110° C. and express the loss in weight as moisture.

Paste.—Heat about 100 grams in the oven at 90–100° C. until dry enough to powder readily and determine the loss in weight. Powder this partly dried sample and determine the remaining moisture in 2 grams as for Powder above. Determine CO_2, as directed later, both in the original paste and in this partially dried sample. Calculate the total moisture by the following formula:

$$M = \frac{(100-a)\ (b+c)}{100} + a - d,$$

in which M = percentage total moisture in original paste;
a = percentage loss in weight of first drying;
b = percentage loss in weight of second drying;
c = percentage CO_2 in paste after first drying;
and d = percentage total CO_2 in original paste.

Carbon Dioxide. *Apparatus.*—This consists of a 200-cc. Erlenmeyer flask closed with a 2-hole stopper; one of these holes is fitted with a dropping funnel, the stem of which extends almost to the bottom of the flask; the outlet of a condenser, which is inclined upward at an angle of 30° from the horizontal, passes downward through the other hole. The upper end of the condenser is connected with a $CaCl_2$ tube which in turn is connected with a double U-tube filled in the middle with pumice fragments, previously saturated with a 20% $CuSO_4$ solution and subsequently dehydrated, and with $CaCl_2$ at either end. Then follow 2 weighed U-tubes for absorbing the CO_2, the first filled with porous soda-lime, and the second, one-third with soda-lime and two-thirds with $CaCl_2$, the latter reagent being placed at the exit end of the train. A Geissler bulb, partly filled with conc. H_2SO_4, is attached to the last U-tube to show the rate of gas flow. An aspirator is connected with the Geissler bulb to draw air through the apparatus. An absorption tower filled with soda-lime is connected with the mouth of the dropping funnel to remove CO_2 from the air entering the apparatus.

Determination.—Weigh 2 grams of the dry powder, or 10 grams of paste, into the Erlenmeyer flask, add about 20 cc. of water, attach the flask to the apparatus, omitting the 2 weighed U-tubes, and draw CO_2-free air through the apparatus until the original air is displaced. Then attach the weighed U-tubes in position as described above, close the stop-cock of the dropping funnel, pour into it 50 cc. of dil. HCl (1 : 4), reconnect with the soda-lime tower, and let the acid flow into the Erlenmeyer flask, slowly if there is much CO_2, rapidly if there is little. When effervescence diminishes, place a low Bunsen flame under the flask and start the flow of water through the condenser, letting a slow current of air flow through the apparatus at the same time. Maintain a steady but quiet ebullition, and a slow air current through the apparatus. Boil for a few minutes after water has begun to condense in the condenser, then remove the flame and

continue the aspiration of air at the rate of about 2 bubbles per second until the apparatus is cool. Disconnect the tared absorption tubes, cool in the balance case and weigh. The increase in weight is CO_2.

Copper.—*Electrolytic Method.*—Dissolve 2 grams of the dry powdered sample in about 75 cc. of water and 20 cc. of conc. HNO_3 in a 250-cc. beaker. Dilute to 200 cc., and electrolyze as described in the method for Brass and Bronze (p. 182). Calculate the percentage of Cu in the sample. Test the solution after electrolysis to make sure all Cu has been removed.

Thiosulfate Method.—Dissolve 2 grams of the powdered sample in about 25 cc. of dil. HNO_3 (1:4), dilute to 50 cc. and add conc. NH_4OH in excess. Boil until the excess of NH_3 is removed, add (without filtering) 3–4 cc. of glacial acetic acid, cool and add 10 cc. of 30% KI solution. Titrate with 0.1 N thiosulfate solution (see below) until the brown color becomes faint, then add starch indicator and continue the titration cautiously until the blue color due to free I has entirely vanished. From the titration calculate the percentage of Cu in the sample.

Standardization of Thiosulfate Solution.—Weigh accurately about 0.25 gram of pure Cu foil and place in a 250-cc. flask. Warm with 5 cc. of dil. HNO_3 (1 : 1) until dissolved. Dilute to 50 cc., boil to expel red fumes, add 5 cc. of strong bromine water and boil until the Br is all driven off. Remove from the heat and add a slight excess of conc. NH_4OH. (About 8–9 cc. are required.) Again boil until the excess of NH_3 is removed as shown by partial precipitation and a change in color of the liquid. Add a slight excess (3 or 4 cc.) of glacial acetic acid and boil for a minute. Cool to room temperature, add 10 cc. of 30% KI solution and titrate with the 0.1 N thiosulfate solution as in the previous paragraph. The blue color changes toward the end to a faint lilac, and if at this point the thiosulfate is added drop by drop and a little time allowed after each addition, the end-point may easily be determined within 1 drop. One cc. of the thiosulfate should be equivalent to about 0.0063 gram of Cu.

Reference.—Association of Official Agricultural Chemists: "Methods of Analysis," 61 (1925).

BORDEAUX MIXTURE WITH PARIS GREEN AND LEAD ARSENATE

General.—Bordeaux Mixture is often mixed with other insecticides and sold under various names. The following procedures are those of the Association of Official Agricultural Chemists.

Bordeaux Mixture with Paris Green

Moisture and Carbon Dioxide (Official).—These are determined as in Bordeaux Mixture.

Copper. *Electrolytic Method (Official).*—Weigh 1 gram of the powdered sample into a small beaker. Add 5 cc. of HBr (about 1.3 sp. gr.) and 15 cc. of conc. HCl and evaporate to dryness to remove As. Repeat the treatment, add 20 cc. more of conc. HCl and again evaporate to dryness. Add to the residue 25 cc. of approximately 2 N HCl (made by diluting 166 cc. of conc. HCl to 1 liter), heat to boiling, filter at once to remove any SiO_2, and wash with hot water to a volume of 125 cc. Pass in H_2S until precipitation is complete. Filter and wash the precipitate thoroughly with 0.5 N HCl saturated with H_2S. Transfer the filter and precipitate to a 400-cc. Pyrex beaker and completely oxidize all organic matter by heating with 4 cc. of conc. H_2SO_4 and a little fuming HNO_3. Remove all the HNO_3 by heating to copious white fumes of SO_3 on the hot plate. Cool, add 2–3 cc. of water and again heat to white fumes. Cool, add 50 cc. of water and let stand 1 hour. If any precipitate forms ($PbSO_4$), add 100 cc. of 95% alcohol and let stand several hours, preferably overnight. Filter through a Gooch crucible, wash the precipitate in the crucible about ten times with acidified alcohol (100 cc. of water, 200 cc. of 95% alcohol and 3 cc. of conc. H_2SO_4), and then once with 95% alcohol.

Evaporate the filtrate and washings from the $PbSO_4$ precipitate (or the H_2SO_4 solution, if no precipitate formed) to fuming; add a few cc. of fuming HNO_3 to destroy organic matter and continue evaporation to a volume of about 3 cc. Take up with about 100 cc. of water, add 1 cc. of conc. HNO_3 and filter, if necessary. Wash into a 150-cc. beaker and electrolize, using a weighed rotating cathode and a current of about 3 amperes. After all the Cu has been deposited, which requires about 30 minutes, wash the deposit with water by siphoning while the current still flows. Then turn off the current, rinse the cathode

with alcohol, dry in the oven for a few minutes and weigh the copper deposit. Calculate the percentage of Cu in the sample.

Thiosulfate Method (Official).—Proceed as above to the point where the final evaporation of the solution to a volume of about 3 cc. has been accomplished. Take up in 50 cc. of water, add conc. NH_4OH in excess and complete the determination as under the thiosulfate method for Cu in Bordeaux Mixture (p. 73).

Total Arsenic (Official).—Proceed as directed for Total Arsenic in Paris Green (p. 76), using 2 grams of the sample and calculating the results as As_2O_3.

Total Arsenious Oxide (Tentative).—Proceed as directed for Total Arsenious Oxide in Paris Green (p. 78), using 0.5–1.0 gram of the sample.

Water-soluble Arsenious Oxide (Tentative).—Proceed as described under Water-soluble Arsenious Oxide in Paris Green (p. 78), using 2 grams of the sample, and slightly acidify with dil. HCl (1:4) before adding the excess of $NaHCO_3$.

Bordeaux Mixture with Lead Arsenate

Moisture and Carbon Dioxide (Official).—Proceed as above described.

Copper (Official).—Proceed as above described, using either the electrolytic or the thiosulfate method.

Lead Oxide (Official).—Follow the procedure for the preliminary treatment of the sample under the Electrolytic Method for copper above. In this case of course the $PbSO_4$ is filtered on a weighed Gooch crucible and finally dried at 200° C. to constant weight. The Gooch crucible should be put through the same treatment with acidified alcohol, etc. before filtering the $PbSO_4$ in it. Calculate results to PbO.

Calculation.—$PbSO_4 \times 0.7360 = PbO$.

Total Arsenic (Official).—Proceed as directed under Total Arsenic in Paris Green (p. 73), using 2 grams of the sample and calculating results as As_2O_5.

Water-soluble Arsenic Oxide (Tentative).—Proceed as directed under Water-soluble Arsenic Oxide in Lead Arsenate (p. 70).

Reference.—Association of Official Agricultural Chemists: "Methods of Analysis," 63, 64 (1925).

PARIS GREEN

General.—Paris Green is the aceto-arsenite of copper. The theoretical composition is: As_2O_3 58.55%, CuO 31.39%, acetic acid 11.84%. The commercial material, however, always contains more or less Na_2SO_4, but in good samples the amount should not be much over 1%. It is also sometimes adulterated with $CaSO_4$.

The following procedures are the methods of the Association of Official Agricultural Chemists.

Moisture (Official).—Dry 2 grams at 105–110° C. to constant weight and report the percentage loss as Moisture.

Total Arsenic (Official).—(Arsenic present as arsenate is titrated as As_2O_3. Cannot be used in the presence of nitrates.)

Reagents.—(*a*) *Starch Indicator.*—Mix about 2 grams of finely powdered potato starch with cold water to a thin paste; pour into about 200 cc. of boiling water, stirring constantly; and immediately discontinue heating.

(*b*) *Standard Arsenious Oxide Solution.*—Dissolve 4 grams of pure As_2O_3 in a beaker by boiling with about 300–400 cc. of water containing 20 cc. of conc. H_2SO_4; cool, transfer to a liter volumetric flask and dilute to the mark.

(*c*) *Standard Iodine Solution.*—Prepare an approximately 0.05 N solution as follows: Mix intimately 6.35 grams of pure iodine with twice its weight of pure KI. Dissolve in a small amount of water, filter and dilute the filtrate to 1 liter in a volumetric flask. Standardize against (*b*) above as follows: Pipette 50 cc. of the As_2O_3 solution into an Erlenmeyer flask, dilute to about 200 cc., neutralize with $NaHCO_3$, add 4–5 grams in excess, and add the standard iodine solution from a burette, shaking the flask continuously, until the yellow color disappears slowly from the solution. Then add 5 cc. of the starch indicator and continue adding the iodine solution, drop by drop, until a permanent blue color is obtained. Calculate the value of the standard iodine solution in terms of As_2O_3 and of As_2O_5 (1 gram of $As_2O_3 = 1.1617$ gram of As_2O_5). Occasionally restandardize the iodine against freshly prepared As_2O_3 solution.

Apparatus.—The apparatus is shown in Fig. 4. The 500-cc. distillation flask rests on a metal gauze which fits over a circular

hole in a heavy sheet of asbestos board. The two Erlenmeyer flasks are of 500-cc. capacity and contain 40 and 100 cc. of water, respectively. The volume in the first flask should not exceed 40 cc., otherwise there may be a loss of arsenic. Both flasks should be placed in a pan and kept surrounded with cracked ice and water or cold circulating water.

DETERMINATION.—Weigh an amount of the sample containing not over 0.4 gram of metallic As, and wash into the distillation flask by means of 100 cc. of conc. HCl. Add 5 grams of cuprous chloride and distill.

When the volume in the distillation flask is reduced to about 40 cc., add 50 cc. more of conc. HCl by means of the dropping funnel

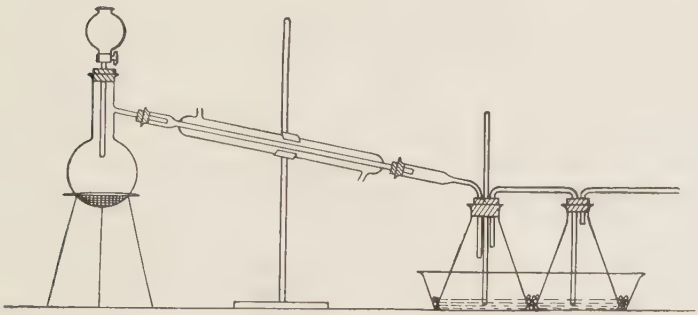

FIG. 4.—Apparatus for Determining Arsenic in Paris Green.

and continue distillation, repeating the additions of 50-cc. portions of HCl, until 200 cc. of the acid distillate have passed over. Then wash down the condenser and all connecting tubes carefully, transfer these washings and contents of the Erlenmeyer flasks to a liter volumetric flask and dilute to the mark. Mix thoroughly, pipette 200 cc. into an Erlenmeyer flask and nearly neutralize with a 40% solution of NaOH, using a few drops of phenolphthalein indicator and keeping the solution well cooled. If the neutral point is passed, make slightly acid with conc. HCl.

Continue as directed under Reagents (*c*), beginning with "neutralize with $NaHCO_3$." From the titration calculate the total arsenic in terms of As_2O_3.

NOTE.—In case the regular 0.1 N iodine solution of the laboratory is used, the amount can be calculated from 1 cc. 0.1 N iodine = 0.004948 gram As_2O_3. In this case take a 400-cc. aliquot of the distillate for titration.

Total Arsenious Oxide (Official).—(The following method determines As, and Sb if present, as the -ous oxides, As_2O_3 and Sb_2O_3, respectively. Ferrous and cuprous salts vitiate the results.)

Reagents.—The reagents and solutions are the same as those described above under Total Arsenic.

Determination.—Weigh 0.3 gram of the sample, wash into an Erlenmeyer flask with 10–15 cc. of dil. HCl (1:4) followed by about 100 cc. of water, and heat on the steam bath only long enough for complete solution, at a temperature not exceeding 90° C. Cool, neutralize with $NaHCO_3$, add 4–5 grams in excess, and then sufficient 25% NH_4Cl solution to dissolve the precipitated copper. Dilute somewhat and titrate as directed under Total Arsenic above. A correction must be applied for the amount of iodine solution necessary to produce a blue color with starch in the presence of copper (using an equivalent weight of copper sulfate). From the corrected number of cc. of the standard iodine solution used calculate the percentage of As_2O_3 in the sample.

Sodium Acetate-soluble Arsenious Oxide (Tentative).

REAGENTS.—(*a*) *Sodium Acetate Solution.*—Prepare a solution containing 12.5 grams of $NaC_2H_3O_2 \cdot 3H_2O$ in each 25 cc.

The other reagents are described under Total Arsenic.

DETERMINATION.—Place 1 gram of the sample in a 100-cc. volumetric flask and boil for 5 minutes with 25 cc. of the sodium acetate solution. Dilute to the mark, shake, and pass through a dry filter paper. Titrate an aliquot of this filtrate with standard iodine solution as directed under Total Arsenic above. Calculate the amount of As_2O_3 present and express the result as percentage of Sodium Acetate-soluble As_2O_3.

Water-soluble Arsenious Oxide (Official).

REAGENTS.—Same as for Total Arsenic.

DETERMINATION.—To 1 gram of the sample in a liter Florence flask add 1 liter of recently boiled water which has been cooled to 32° C. Stopper the flask and place in a water bath kept at 32° C.

by means of a thermostat. Digest for 24 hours, shaking hourly for 8 hours during this period.* Filter through a dry filter and titrate 250 cc. of the filtrate as directed under Total Arsenic above, first adding 4–5 grams of $NaHCO_3$. Correct for the amount of the standard iodine necessary to produce the same color, using the same reagents and volume. Calculate the amount of As_2O_3 present and express the result as percentage of Water-soluble As_2O_3.

Total CuO.—Electrolytic Method (Official).—Treat 2 grams of the sample in a beaker with 100 cc. of water and about 2 grams of NaOH and boil thoroughly until all Cu is precipitated as Cu_2O. Filter, wash well with hot water, dissolve the precipitate in hot dil. HNO_3 (1:4), cool, transfer to a 250-cc. volumetric flask and dilute to the mark. Use 50–100 cc. of this solution for the electrolytic determination of Cu either with a rotating cathode and stationary anode in a beaker, or with a rotating spiral anode, using a weighed 150-cc. platinum dish for the cathode, and a current of about 3 amperes. After all the Cu is deposited, wash the deposit with water by siphoning, then rinse with alcohol, dry for a few minutes in an oven, weigh and calculate to percentage of CuO.

Calculation.—$Cu \times 1.2517 = CuO$.

Thiosulfate Method (Official).—Determine Cu in another aliquot of the HNO_3 solution of the Cu_2O prepared as described above, by titrating with 0.1 N thiosulfate solution as described under Copper in Bordeaux Mixture (p. 73). Calculate to percentage of CuO.

Reference.—Association of Official Agricultural Chemists: "Methods of Analysis," 53 (1925).

LIME SULFUR SOLUTION

General.—Lime sulfur solutions are made by boiling, either by direct heat or by live steam, sulfur and freshly slaked lime in water. The resulting solution contains considerable amounts of polysulfides and thiosulfate and very small amounts of sulfate and sulfite. In commercial practice, 1 part of lime and 2 parts of sulfur are used. Lime comparatively free from MgO must be employed.

* See note on page 69 under Total Water-soluble Matter in Lead Arsenate.

The sample for analysis should be kept tightly stoppered and not exposed to air, as it will very easily precipitate free sulfur.

The determinations below marked "Official" are those of the Association of Official Agricultural Chemists.

Specific Gravity.—Determine the sp. gr. with a Westphal balance at 15.5° C. (60° F.) and calculate to degrees Baumé; or if there is sufficient sample at hand, determine the gravity directly with a Baumé hydrometer.

Total Sulfur (Official).—Measure and accurately weigh from a stoppered weighing bottle about 10 cc. of the clear sample. Transfer to a 250-cc. volumetric flask, partly filled with recently boiled and cooled water, and dilute to the mark with the same water. Mix thoroughly and transfer to a number of small bottles, filling them completely and avoiding exposure of the solution to air as much as possible. Stopper the bottles, seal with paraffin and preserve in a dark, cool place. For the determination of total sulfur and for other determinations (unless otherwise directed) use 10-cc. aliquots of this solution.

Dissolve 2–3 grams of Na_2O_2 in 50 cc. of cold water in a 250-cc. beaker. Transfer a 10-cc. aliquot of the above solution to the Na_2O_2 solution, keeping the tip of the pipette just beneath the surface of the liquid until necessary to raise it for drainage at the end. Use a clean dry pipette for measuring each portion. Cover the beaker immediately with a watch glass and warm on the steam bath, with occasional stirring, until all S is oxidized to sulfate, as shown by the disappearance of the yellow color. Dilute, acidify with dil. HCl, evaporate to dryness, treat with water acidified with HCl, boil, and filter to remove silica, if present. Dilute the filtrate to 300 cc., add 50 cc. of conc. HCl, heat to boiling and precipitate with excess of 10% $BaCl_2$ solution slowly and stirring constantly. The $BaCl_2$ should be added at such a rate that about 4 minutes are required for running in the necessary quantity (11 cc. for 1 gram of $BaSO_4$). The rate is best regulated by attaching a suitable capillary tip to a burette containing the $BaCl_2$ solution. Evaporate to dryness on the steam bath, take up with hot water, filter through a quantitative filter paper, wash until free from Cl and ignite to constant weight over a Bunsen burner. Weigh as $BaSO_4$ and calculate to sulfur.

Previous to use, test all reagents for sulfur and, if present, make corrections accordingly.

CALCULATION.—$BaSO_4 \times 0.1373 = Sulfur$.

Sulfur as Polysulfides.—Pipette 10 cc. of the solution described above into a small beaker and add about 30 cc. of water. Then run into the solution from a burette 0.1 N HCl, drop by drop, with constant stirring, until the yellow tint has practically disappeared. Add 2 drops of methyl orange and continue the addition of acid until the first permanent pink color appears. (After standing for some time this tint will gradually disappear.) The solution will be milky white from finely divided S present, but it is not difficult to ascertain the exact end-point of the reaction. Let the solution stand a few moments to permit S to settle and collect together. Filter on a weighed Gooch crucible, wash thoroughly, dry at about 40° C. and weigh directly as free S. This represents S combined in the form of polysulfides.

NOTES.—(1) Precipitation of S by means of weak acid does not decompose thiosulfate in solution.

(2) An optional method of determining the sulfur is as follows: Filter on a small filter paper instead of on a Gooch crucible, and after thoroughly washing, gently boil the paper and contents in 50 cc. of 10% KOH solution until all sulfur is dissolved. After cooling add 50 cc. of a 3% solution of H_2O_2, free from sulfates. Heat on the steam bath for exactly 30 minutes and then acidify with HCl and precipitate with $BaCl_2$ in the usual manner. Finally weigh as $BaSO_4$. Run a blank on the KOH solution and subtract any sulfur found.

Sulfur as Sulfide (Official).—To 10–15 cc. of water in a small beaker add, in the manner described under Total Sulfur, a 10-cc. aliquot of the solution prepared as there described. Calculate the quantity of ammoniacal $ZnCl_2$ solution (see notes) necessary to precipitate all the S in the aliquot and add a slight excess. Stir well, filter at once, and wash the precipitate twice with cold water.

Transfer the filter paper and precipitate to the beaker in which the precipitation was made; cover with water, disintegrate the paper with a glass rod and add about 3 grams of Na_2O_2, keeping the beaker well covered with a watch glass. Warm on a steam bath with frequent shaking until all S is oxidized to sulfate, adding more Na_2O_2 if necessary. Make slightly acid with dil.

HCl, filter to remove shreds of filter paper, wash thoroughly with hot water and determine sulfur in the filtrate exactly as under Total Sulfur above.

This gives both monosulfide and polysulfide sulfur. Subtract the polysulfide sulfur as previously determined and report the difference as (mono) Sulfide Sulfur.

NOTES.—(1) *Ammoniacal Zinc Chloride Solution*—Dissolve 50 grams of pure $ZnCl_2$ in about 500 cc. of water. Add 125 cc. of conc. NH_4OH to redissolve the precipitate first formed; then add 50 grams of NH_4Cl and dilute to 1 liter. Each cc. of this solution is equivalent to 0.0118 gram of sulfur.

(2) Blank determinations of the amount of S in the reagents used should be made and corrections applied.

(3) The amount of sulfur as polysulfide is almost always quite close to 3.5 times the amount of sulfur as sulfide. This shows that the polysulfide in solution is not one compound only, but probably a mixture of CaS_4 and CaS_5.

Sulfur as Thiosulfate (Official).—Add 50 cc. of the solution prepared as for Total Sulfur to 50 cc. of water in a 250-cc. volumetric flask, in the manner previously described. Add ammoniacal $ZnCl_2$ solution until in slight excess and make up to the mark. Shake thoroughly and filter through a dry filter. To 200 cc. of the filtrate add methyl orange and exactly neutralize with 0.1 N HCl. Titrate this neutral solution with 0.1 N iodine, using a few drops of starch paste as indicator. From the amount of iodine solution required calculate the sulfur present as thiosulfate.

CALCULATION.—1 cc. 0.1 N iodine = 0.006413 gram sulfur.
= 0.01581 gram $Na_2S_2O_3$.

Sulfur as Sulfate (Official).—To the solution from the determination of thiosulfate add a slight excess of HCl. Heat to boiling, add slowly with constant stirring a slight excess of 10% $BaCl_2$ solution, boil for 30 minutes and let stand overnight. Filter, ignite and weigh as $BaSO_4$. From this weight calculate the sulfur and report as sulfate sulfur.

NOTE.—In case any sulfite is present, the determination of thiosulfate will be too high. As calcium sulfite is nearly insoluble, however, it will not be present in more than traces and the error from this cause will be negligible. It is unusual for the combined sulfate and sulfite to amount to more than a small fraction of 1%.

Total Lime (Official).—To 25 cc. of the solution prepared as under Total Sulfur add 10 cc. of conc. HCl; evaporate to dry-

ness on the steam bath, treat with water and a little dil. HCl, warm until all the $CaCl_2$ is dissolved, and filter from S and any SiO_2 that may be present. Oxidize the filtrate by boiling with a little conc. HNO_3; make ammoniacal, filter from Fe and Al if present; heat to boiling and precipitate the Ca with an excess of saturated $(NH_4)_2C_2O_4$ solution. Boil until the CaC_2O_4 is granular and let stand 1 hour. Filter, wash with hot water and ignite over a blast lamp to constant weight. Weigh as CaO. (The CaC_2O_4 may be titrated with 0.1 N $KMnO_4$ solution in the usual way, if desired, instead of igniting it.)

REFERENCE.—Association of Official Agricultural Chemists: "Methods of Analysis," 68 (1925).

CORROSIVE SUBLIMATE IN MEDICATED GAUZE

Weigh 30 grams of gauze, or the whole sample if less than this, and place in a 200-cc. separatory funnel; pack firmly, and add 200 cc. of warm dil. HCl (15 cc. of conc. HCl per liter). Let the acid drain slowly into a 1000-cc. beaker, about 2 or 3 drops per second. When completely drained, add 100 cc. more of the warm dil. HCl, and continue the draining operation until complete. Repeat 5 times, so that the gauze is washed with a total of 800 cc. of acid.

Pass H_2S through the solution for 1 hour and let stand overnight. Filter through a weighed filter or Gooch crucible. Wash six times with water, and then three times with 95% alcohol. Stopper the bottom of the funnel with a small cork; add CS_2 sufficient to cover the precipitate of HgS completely, and let stand for 0.5 hour. Remove the stopper and let drain. Wash once with CS_2, and three times with alcohol. Dry and weigh.

In case a Gooch crucible is used, set the crucible in a beaker containing sufficient CS_2 to cover the precipitate. Let stand 0.5 hour, etc. Calculate parts of $HgCl_2$ per thousand parts of gauze.

CALCULATION. $\frac{W \times 1.167 \times 100}{S}$ = parts $HgCl_2$ per thousand,

where W = weight of HgS, and S = weight of gauze.

NOTE.—This is the method prescribed by the U. S. Government for testing medicated surgical dressings.

ASBESTOS MAGNESIA PIPE COVERING

General.—This material consists of a molded mixture of long-fibered asbestos with light magnesium carbonate. The specifications on which it is generally purchased are as follows:

Long-fibered asbestos, not less than 10%.
Magnesium carbonate, not less than 85%.

The magnesium carbonate is calculated to the empirical formula $Mg(OH)_2 \cdot 4MgCO_3 \cdot 4H_2O$. The commercial carbonate from which the material is made usually contains about 2.5% of hygroscopic moisture, less than 1% of $Fe_2O_3 + Al_2O_3$, and seldom more than 3% of $CaCO_3$.

The following procedures are essentially those adopted in 1922 by the Magnesia Association of America:

Preparation of Sample.—Since the asbestos and magnesium carbonate do not adhere very strongly to each other, it is necessary to use care in sampling this material. A considerable number of representative lumps should be taken for the analysis and these lumps should not be shaken nor squeezed on account of danger of loss of carbonate. If it is attempted to grind up the whole sample and quarter it down, some magnesium carbonate is very likely to be lost. For accurate results the following porcedure is recommended:

Cut 10 pieces from different portions of the sample, using a very sharp, thin-bladed knife and taking great care to slice the asbestos fibers off clean and to avoid pulling them out of the magnesia. Then trim down each piece to a cubical shape, slicing off any projecting fibers cleanly. Finally crush the cubes and mix thoroughly. Quarter down, if necessary, to approximately 25 grams and preserve in a straight-sided, wide-mouthed glass jar. Shake the jar and contents thoroughly just before taking the sample for analysis.

Asbestos.—Shake* out from the jar and accurately weigh about 5 grams of the prepared sample into a 350-cc. beaker. Add 100 cc. of water and 2 drops of methyl orange indicator and then approximately normal HCl, with stirring, until all the carbonate has dissolved and a permanent pink color has just appeared. (This will usually require about 25 cc. for each gram of the

* Do not handle with the fingers or any implement which might cause a pinching action. Simply shake out the proper amount of sample.

sample.) Filter off the asbestos at once on a dried and weighed Gooch crucible and wash thoroughly with cold water, saving the filtrate. Dry the residue of asbestos to constant weight at 105–110° C.

Iron Oxide and Alumina.*—To the filtrate and washings from the previous determination add 5 cc. of conc. HCl for each gram of sample and heat to boiling. Add a slight excess of dil. NH_4OH and boil until the odor of NH_3 is nearly gone. Filter and wash with hot water; ignite strongly in a weighed platinum crucible, cool in a desiccator, and weigh as $Fe_2O_3+Al_2O_3$.

Calcium Carbonate.—Heat to boiling the filtrate from the $Fe_2O_3+Al_2O_3$ in a 750-cc. beaker. Make slightly acid with HCl, dilute to 500 cc. (if necessary), add about 25 cc. of $(NH_4)_2C_2O_4$ reagent and then a slight excess of NH_4OH. Boil for 5 minutes and let cool. Decant the bulk of the solution through a filter into a liter volumetric flask, then collect the precipitate on the filter and wash two or three times with 50-cc. portions of cold water. Dissolve the precipitate on the filter in hot dil. HCl (10%), catching this solution in the beaker in which the precipitation was originally made. Wash the filter thoroughly with cold water. Heat the filtrate and washings in the beaker to boiling, add a few cc. of $(NH_4)_2C_2O_4$ solution and then a slight excess of NH_4OH. Let cool, filter, and add this filtrate to the filtrate from the first precipitation in the liter volumetric flask. Wash the precipitate with cold water, discarding the washings. Ignite in a weighed platinum crucible over a blast lamp, cool in a desiccator, and weigh rapidly as CaO. Calculate to $CaCO_3$.

CALCULATION.—$CaO \times 1.785 = CaCO_3$.

Magnesium Carbonate.—Dilute the mixed filtrates from the $CaCO_3$ determination to 1 liter in the flask and pipette 100 cc., representing about 0.5 gram of the original substance, into a 500-cc. beaker. Dilute to about 400 cc. and add a slight excess of HCl. Then add 15–20 cc. of a saturated solution of $NaNH_4HPO_4$ and a considerable excess of NH_4OH. Stir until precipitation is complete and let stand overnight in the cold. Decant the bulk of the liquid through a Gooch crucible which has been ignited and weighed. Dissolve the precipitate in the beaker in the least possible amount of dil. HCl, add a few drops of phos-

* See note 1.

phate solution and then NH_4OH in slight excess, with stirring as before. Let stand 6 hours and filter through the same Gooch crucible, washing with dil. NH_4OH (1 : 10). Ignite gently at first and then in a blast for 20-minute intervals until constant. Weigh as $Mg_2P_2O_7$ and calculate to $Mg(OH)_2 \cdot 4MgCO_3 \cdot 4H_2O$.

CALCULATION.—$Mg_2P_2O_7 \times 0.837 = Mg(OH)_2 \cdot 4MgCO_3 \cdot 4H_2O$.

Hygroscopic Moisture.—Dry a 2-gram sample in a watch glass or flat dish to constant weight at 105° C. Calculate the loss in weight as hygroscopic moisture.

NOTES.—(1) It is customary to determine only the asbestos and the magnesium carbonate and report the remainder as Moisture and Impurities. In this case of course the precipitates obtained under Iron Oxide and Alumina and under Calcium Carbonate need not be weighed. In fact it is not necessary to remove the $Fe_2O_3 + Al_2O_3$ precipitate before precipitating the CaC_2O_4 and they may be filtered off together.

(2) The factor 0.837 for converting $Mg_2P_2O_7$ to the carbonate is an empirical one and is claimed to give results nearer the average composition than the theoretical factor 0.840.

(3) There are several basic carbonates of magnesium known which vary considerably in composition. If satisfactory results cannot be obtained by the above procedure, it indicates that a magnesium carbonate has been used of different composition than usual. In such a case a complete ultimate analysis may be necessary, determining asbestos, hygroscopic moisture, loss on ignition, CO_2, $Fe_2O_3 + Al_2O_3$, CaO and MgO. In calculating the composition it may be assumed that the asbestos itself would lose 14% on ignition. After calculating the CaO to $CaCO_3$ and the remainder of the CO_2 to $MgCO_3$, the remainder of the MgO should be calculated to $Mg(OH)_2$. The combined water of crystallization of the basic magnesium carbonate is then calculated from the loss on ignition, after subtracting from the latter the CO_2, water combined as $Mg(OH)_2$ and loss due to asbestos. This method is very accurate but is time consuming and expensive for routine analysis.

Calculations.—$CaO \times 1.7847 = CaCO_3$.
$CO_2 \times 1.9164 = MgCO_3$.
$MgO \times 1.4469 = Mg(OH)_2$.
$Mg(OH)_2 \times 0.3088 = H_2O$

REFERENCE.—*J. Ind Eng. Chem.*, **15**, 50 (1923).

CHAPTER III

GENERAL ORGANIC ANALYSES

NITROGEN

General.—The principle of the determination of nitrogen in organic materials and in fertilizers is its conversion into NH_3 and a determination of the amount of NH_3 so formed. The method to be employed depends upon whether or not nitrates are present. In every case a blank should be carried out to correct for the presence of small amounts of nitrogen in the reagents employed. In running the blank, employ the same amount of each reagent as is used in the determination.

In this laboratory we have found the Gunning methods preferable to the Kjeldahl for most substances. (See general notes on p. 89.)

Methods to Be Used in the Absence of Nitrates

Kjeldahl Method.*—Place 0.7–3.5 grams of the substance to be analyzed (depending upon the N content) in a 500-cc. pear-shaped digestion flask. Add approximately 0.7 gram of mercuric oxide,† or its equivalent of metallic Hg, and 20–30 cc. of conc. H_2SO_4. From 0.1 to 0.3 gram of crystallized $CuSO_4$ may also be used in addition to the Hg or in place of it. Place the flask in an inclined position and heat gently below the boiling point of the acid until frothing has ceased. (A small piece of paraffin may be added to prevent extreme foaming.) Then raise the heat until the acid boils briskly and digest for 4 hours after the mixture is colorless, or nearly so.

After cooling, dilute with about 200 cc. of water and add a few pieces of granulated zinc or pumice stone and 25 cc. of K_2S solu-

* For ordinary work 0.5 N acid is recommended. For work in determining very small amounts of nitrogen 0.1 N acid is recommended.

† If HgO is used, it should be prepared in the wet way but not from $Hg(NO_3)_2$.

tion (40 grams of commercial K_2S* in 1 liter of water) with shaking. Next add 50 cc. of a saturated solution of NaOH (free from N compounds) or more if necessary to make the solution strongly alkaline, pouring it down the side of the flask so that it does not mix at once with the acid solution. The NaOH solution should have a sp. gr. of 1.43–1.48 and is prepared by dissolving 450 grams of commercial NaOH in 1 liter of water.

Connect the flask by means of a Kjeldahl connecting bulb with the condenser, the tip of which extends below the surface of the standard acid in the receiver; mix the contents well by swirling and then distill until all the NH_3 has passed over, collecting the distillate in an excess of standard acid. As a general rule, 50 cc. of 0.1 N HCl or 10 cc. of 0.5 N will be sufficient. It should have cochineal, methyl orange, or methyl red indicator (see general note 3) added to it before the distillation starts; and if the color changes before it is completed, the determination should be repeated, using either less of the original material or more of the standard acid. The first 150 cc. of the distillate will generally contain all the NH_3. The distillation usually requires 40–90 minutes. Wash down the condenser with distilled water and titrate the excess of standard acid with 0.1 N alkali.

The K_2S removes all the Hg from the solution and thus prevents the formation of mercuro-ammonium compounds, which are not completely decomposed by the caustic. The addition of Zn gives rise to an evolution of hydrogen and prevents violent bumping.

Gunning Method.—The apparatus used is the same as that employed in the Kjeldahl method.

Place the substance to be analyzed in a 500-cc. digestion flask, using 0.7–3.5 grams according to the proportion of N. Add 10 grams of powdered K_2SO_4 or anhydrous Na_2SO_4 (use Baker's C. P. special, free from nitrogen) and 25 cc. of conc. H_2SO_4. Add also about 0.2 gram of crystallized $CuSO_4$ or 0.1 gram of copper wire. Conduct the digestion exactly as in the Kjeldahl process, starting with a temperature below the boiling point and increasing the heat gradually until frothing ceases. Digest for 4 hours after the mixture is colorless, or nearly so. Do not add K_2S. Cool, dilute, add an excess of NaOH, distill and titrate as in the Kjel-

* A solution of 40 grams of sodium sulfide or 80 grams of sodium thiosulfate in a liter of water may be used in place of the K_2S solution.

dahl method. In neutralizing, it is advisable to add a few drops of methyl orange or litmus indicator by which one can tell when an excess of NaOH has been added.

NOTES.—(1) It is well for convenience to use the same amount of H_2SO_4 each time for digestion and to determine how much of the strong NaOH is necessary to neutralize this amount of acid, marking the amount on the bottle containing the NaOH.

(2) If copper wire of the same size is always used, it can easily be determined how long a piece will weigh 0.1 g. and then cut up a number of pieces of the proper length. The use of copper wire has not yet been made an official method of the A. O. A. C. but sufficient work has been done to show that it gives accurate results.

Kjeldahl-Gunning-Arnold Method.—Place 0.7–3.5 grams of the material (according to the N content) in the digestion flask. Add 15–18 grams of powdered K_2SO_4 or anhydrous Na_2SO_4, 1 gram of $CuSO_4$ or approximately 0.7 gram of HgO (or its equivalent of metallic Hg), and 25 cc. of conc. H_2SO_4. Heat gently until frothing ceases, then boil briskly and continue digestion for at least 2 hours after the liquid is colorless or nearly so. Cool, dilute with about 200 cc. of water, add 50 cc. of K_2S solution,* make strongly alkaline with NaOH solution and complete the distillation as under the Kjeldahl method.

GENERAL NOTES.—(1) A blank determination should be run, using all reagents in the same amount as in the regular determination.

(2) We have found the Gunning methods the most convenient for use but either method gives accurate results, and the Kjeldahl is quicker.

(3) It is generally recommended that cochineal or methyl red be used in titrating back the excess of acid, but accurate results can be obtained by using methyl orange as follows:

To a container of similar size and shape to that containing the distillate, add an amount of distilled water equal to the volume of the distillate and add the same number of drops of indicator (two or three are sufficient) as were added to the standard acid. Then titrate until the color matches the color of the distilled water containing the methyl orange. (The titration of the blank on the reagents should, of course, be carried to the same end point.)

(4) With certain materials it will be necessary to add considerably more H_2SO_4 than the amounts given above. In this case, care must be taken that the mixture in the flask is alkaline before the distillation is started.

(5) Only a moderate excess of the NaOH solution should be added, since considerable excess often causes frothing.

* See footnote on p. 88. The solution need not be added here if the $CuSO_4$ is used in place of the Hg or HgO.

Methods to Be Used in the Presence of Nitrates

The results obtained by these methods give total nitrogen and include the nitrogen of the nitrates.

Modified Kjeldahl Method.—Place 0.7–3.5 grams of the substance in a Kjeldahl digestion flask: (1) Add 30 cc. of conc. H_2SO_4 containing 1 gram of salicylic acid. Shake until thoroughly mixed, let stand for at least 30 minutes and then add 5 grams of crystallized sodium thiosulfate. Or, (2) add to the substance 30 cc. of conc. H_2SO_4 containing 2 grams of salicylic acid, let stand at least 30 minutes with frequent shaking, or until complete solution results, and then add gradually 2 grams of zinc dust, shaking the contents of the flask at the same time. The zinc dust should be an impalpable powder. Granulated Zn or Zn borings will not answer.

Place the flask on the stand for holding digestion flasks and heat over a low flame until all danger from frothing has passed. Then raise the heat until the acid boils briskly and continue boiling until white fumes no longer escape from the flask. This requires about 5–10 minutes. Then add approximately 0.7 gram of HgO or its equivalent in metallic Hg. Continue the boiling until the liquid in the flask is colorless or nearly so. In case the contents of the flask are likely to become solid before this point is reached, add 10 cc. more of conc. H_2SO_4. Complete the determination as described in the Kjeldahl method. Run a blank on all the reagents employed.

Modified Gunning Method.—In a 500-cc. digestion flask place 0.7–3.5 grams of the substance to be analyzed, add 30 cc. of conc. H_2SO_4 containing 1 gram of salicylic acid dissolved in it, shake until thoroughly mixed and let stand for at least 30 minutes with frequent shaking or until complete solution results. Add 5 grams of sodium thiosulfate and heat the solution for 5 minutes. Cool, add 10 grams of powdered K_2SO_4 or anhydrous Na_2SO_4 (Baker's C. P. special) and heat very gently until foaming ceases and then strongly until nearly colorless. Dilute, neutralize and distill as in the Gunning method.

Absolute or Cupric Oxide Method.—By this method the nitrogen is all set free as such and measured in an azotometer. It is not ordinarily employed in commercial analysis but is

described in Association of Official Agricultural Chemists, "Methods of Analysis" (1925), page 9.

Ammoniacal Nitrogen

Magnesia Method.—Place 0.7–3.5 grams of the material, according to the NH_3 content, in a distillation flask with about 200 cc. of water and 5 grams or more of MgO, free from carbonates. Then connect the flask with a condenser by means of a Kjeldahl connecting bulb, distill 100 cc. of the liquid into a measured quantity of standard acid and titrate the excess of acid with standard alkali.

Nitric and Ammoniacal Nitrogen

Reduced Iron Method.—Place 1 gram of the sample in a 500-cc. flask, add about 30 cc. of water and 2–3 grams of reduced iron and, after standing sufficiently long to insure solution of the soluble nitrates and ammonium salts, add 20 cc. of dil. H_2SO_4 (1:1). Shake thoroughly, place a long-stemmed funnel in the neck of the flask to prevent mechanical loss and let stand for a short time until the violence of the reaction has moderated. Heat the solution slowly; then boil for 5 minutes and cool. Add about 100 cc. of water, a little paraffin, and 7–10 grams of MgO, free or nearly free from carbonates. Connect with a condenser such as is used in the Kjeldahl method, using a Kjeldahl connecting bulb, and boil the mixture for about 40 minutes nearly to dryness, collecting the NH_3 in a measured quantity of standard acid, and titrate the excess with standard alkali in the usual way. The nitrogen obtained represents the nitrates plus the ammonium salts contained in the sample.

In the analysis of nitrate salts proceed as above, but use 25 cc. of the nitrate solution (equivalent to 0.25 gram of the sample) with 5 grams of reduced iron. After boiling, add 75 cc. of water and an excess of NaOH solution and complete the determination as above.

Nitrogen in Nitrate Salts

Zinc-Iron Method.—Dissolve 10 grams of the sample in water and dilute to 500 cc. Place 25 cc. of this solution, corresponding

to 0.5 gram of the substance, in a 400-cc. distillation flask. Add 120 cc. of water, 5 grams of well-washed and dried zinc dust, and 5 grams of reduced iron. To the solution add 80 cc. of saturated NaOH solution (see p. 88), connect the flask with the condenser and conduct the distillation simultaneously with the reduction, collecting the NH_3 in excess of standard acid. Continue the distillation until 100 cc. have been distilled and titrate the excess acid with standard alkali. The nitrogen obtained represents the nitrates plus the NH_4 salts present.

Ferrous Sulfate-Zinc-Soda Method.—Place 0.5 gram of the nitrate salt in a 600–700-cc. flask, add 200 cc. of water, 5 grams of powdered zinc, 1–2 grams of ferrous sulfate and 50 cc. of 30% NaOH solution. Connect with the distilling apparatus and distill, collecting the distillate in the usual way in 0.1 N acid and titrating the excess with standard alkali.

Methods for "Available Organic Nitrogen"

Organic Nitrogen Soluble in Neutral Permanganate.—As a preliminary test for the determination of water-insoluble organic N, place 1 gram of the material on an 11-cm. filter paper and wash with water at room temperature until the filtrate measures 250 cc. Dry and determine the N in the residue by the Kjeldahl or Gunning method, making a correction for the N of the filter if necessary.

Place a quantity of the material equivalent to 0.050 gram of water-insoluble organic N as determined above on a moistened 11-cm. filter paper and wash with water at room temperature until the filtrate measures 250 cc. Transfer the insoluble residue with 25 cc. of tepid water to a 400-cc. Griffin low-form beaker. Add 1 gram of Na_2CO_3; mix and add 100 cc. of 2% $KMnO_4$ solution; cover with a watch glass and immerse for 30 minutes in a steam or hot-water bath, keeping the level of the liquid in the beaker below that of the water in the bath. Stir twice at intervals of 10 minutes. At the end of the digestion, remove from the bath, add immediately 100 cc. of cold water and filter through a heavy 15-cm. folded filter. Wash with small quantities of cold water until the filtrate measures about 400 cc. Determine N, in the residue and filter paper by the Kjeldahl or Gunning method,

correcting for any N contained in the paper. The N thus obtained is the inactive water-soluble organic N. Subtract this result from the total water-insoluble organic N to obtain the percentage of water-insoluble organic N soluble in neutral permanganate.

Organic Nitrogen Soluble in Alkaline Permanganate.—PREPARATION OF SAMPLE.—(*a*) *Mixed Fertilizers.*—Place an amount of the sample equivalent to 0.050 gram of water-insoluble organic N, determined as above, on a filter paper and wash with water at room temperature until the filtrate measures 250 cc.

(*b*) *Raw Materials.*—Place an amount of the material equivalent to 0.050 gram of water-insoluble organic N, determined as above, in a small mortar. Add about 2 grams of powdered rock phosphate, mix thoroughly, transfer to a filter paper and wash with water at room temperature until the filtrate measures 250 cc. When much fat or oil is present, it is well to wash with ether before extracting with water.

DETERMINATION.—Dry the residue from the water extract above at a temperature not exceeding 80° C. and transfer from the filter to a 500–600-cc. Kjeldahl distilling flask. Add 20 cc. of water, 15–20 small glass beads or fragments of pumice stone, a piece of paraffin the size of a pea and 100 cc. of alkaline permanganate solution (25 grams of pure $KMnO_4$ and 150 grams of NaOH separately dissolved in water, the solutions cooled, mixed and diluted to 1 liter). Connect with an upright condenser, to the lower end of which a receiver containing standard acid has been attached. Digest slowly for at least 30 minutes below the distillation point with a very low flame, using coarse wire gauze and asbestos paper between the flask and flame. Gradually raise the temperature and after any danger from frothing has passed, distill until 95 cc. of the distillate are obtained, and titrate as usual. When a tendency to froth is noticed, lengthen the digestion period and no trouble will be experienced when the distillation is begun. During the digestion gently rotate the flask occasionally, particularly if the material shows a tendency to adhere to the sides. The N thus obtained is the active water-insoluble organic N.

CALCULATIONS.—The following factors will be found useful in calculating:

1 cc. 0.1 N acid = 0.001401 gram N.
= 0.001703 gram NH_3.
= 0.01011 gram KNO_3.
= 0.002604 gram $(NH_4)_2O$.
= 0.008937 gram casein (N×6.38).
= 0.007844 gram glue (N×5.6).
= 0.008755 gram protein (N×6.25).
= 0.007985 gram protein (N×5.7).*

REFERENCES.—The above methods are all official methods of the Association of Official Agricultural Chemists. See its "Methods of Analysis," 6–12 (1925). See also *J. Am. Leather Chem. Assoc.*, **11**, 454 (1916).

METHYL ALCOHOL

General.—This method applies to the analysis of methyl alcohol (methanol, wood alcohol) to be used for denaturing ethyl alcohol.

The methyl alcohol submitted must be partially purified wood alcohol obtained by the destructive distillation of wood. It must conform to the following analytical requirements:

Color.—It shall not be darker than the color produced by a freshly prepared solution of 2 cc. of 0.1 N iodine diluted to 1000 cc. with distilled water.

Specific Gravity.—It must have a sp. gr. of not more than 0.830 at 60° F. (15.56° C.), corresponding to 91° of Tralles' Scale.

Boiling Point.—100 cc. slowly heated in a flask under conditions as described below must give a distillate of not less than 90 cc. at a temperature not exceeding 75° C. at normal barometric pressure (760 mm.).

Run 100 cc. of wood spirit into a short-necked copper flask of about 180–200-cc. capacity and place the flask on an asbestos plate having a circular opening of 30-mm. diameter. In the neck of this flask is fitted a fractionating tube 12 mm. wide and 170 mm. long, with a bulb just 1 cm. below the side tube, which is connected with a Liebig's condenser having a water jacket not less than 400 mm. long. In the upper opening of the fractionating tube is placed a standardized thermometer, so adjusted that its mercury bulb comes in the center of the bulb. The distillation is conducted in such a manner that 5 cc. pass over in 1

* In wheat products.

minute. The distillate is run into a graduated cylinder, and when the temperature of 75° C. has been reached at the normal barometric pressure of 760 mm. at least 90 cc. shall have been collected.

Should the barometer vary from 760 mm. during the distillation, 1° C. shall be allowed for every variation of 30 mm. For example, at 770 mm. 90 cc. should have distilled at 75.3° C. and at 750 mm. 90 cc. should have distilled at 74.7° C.

Miscibility with Water.—It must give a clear or only slightly opalescent solution when mixed with twice its volume of water.

Acetone Content.—It must contain not more than 20 nor less than 10 grams per 100 cc. of acetone and other substances estimated as acetone when tested by the following (Messinger) method:

With a standardized pipette measure 10 cc. of the sample into a 500-cc. glass-stoppered volumetric flask, make up to the mark with distilled water and mix thoroughly. Pipette out 5 cc. of this solution (with a standardized pipette) and treat with 10 cc. of 2 N NaOH solution. Then add with shaking 50 cc. of 0.1 N iodine solution and 3 minutes after the addition of the iodine make the mixture acid with dil. H_2SO_4. Titrate back the excess of iodine with 0.1 N sodium thiosulfate solution, using a few drops of starch solution as indicator. From 10.3 to 20.7 cc. of 0.1 N iodine solution should be consumed by the spirit.

IMPORTANT.—The solution must be kept at a temperature between 15 and 20° C.

CALCULATION.—Let X = grams of acetone in 100 cc. of spirit,

Y = number of cc. of 0.1 N iodine solution required,

and N = volume of spirit taken for titration;

then, $$X = \frac{Y \times 0.096672}{N}.*$$

Blank Correction.—It is recommended that a blank correction be made as follows:

Weigh accurately from a weighing bottle about 16 grams of Kahlbaum's C. P. acetone into a standardized 100-cc. volumetric flask partially filled with Kahlbaum's C. P. methyl alcohol. Make

* This is the figure given in appendix to *Regulations* 61 (Revised 1925), U. S. Internal Revenue. Using 1925 atomic weights the figure becomes 0.096747.

up accurately to the mark with more of the methyl alcohol. Determine the amount of acetone in this solution, following the method above described. If less acetone is found than was added, add the difference as the blank correction to the acetone found in the sample of denaturant. If more acetone is found in the blank, subtract the difference from that found in the denaturant. Separate blanks should be run with each sample of denaturant, taking care that all the conditions are kept the same.

Esters.—It should contain not more than 5 grams of esters per 100 cc. of spirit, calculated as methyl acetate and determined as follows:

Run 5 cc. of the spirit into a flask and add 10 cc. of N NaOH solution free from carbonates, connect the flask with a return condenser and boil for 2 hours. Instead of digesting at boiling temperature the flask may be allowed to stand overnight at room temperature and then heated on a steam bath for 30 minutes with an ordinary tube condenser. Cool the liquid after digestion and titrate the excess NaOH with N H_2SO_4 and phenolphthalein.

CALCULATION.—Methyl acetate (grams per 100 cc. of spirit)

$$= \frac{0.074 \times \text{cc. of N NaOH consumed} \times 100}{\text{cc. of spirit taken}}$$

$$= 1.48 \times \text{cc. of N NaOH consumed.}$$

Bromine Absorption.—It must contain a sufficient quantity of impurities derived from the wood so that not more than 25 cc. nor less than 15 cc. should be required to decolorize a standard solution containing 0.5 gram of bromine, as follows:

The standard Br solution is made by dissolving 12.406 grams of KBr and 3.481 grams of $KBrO_3$ (which is of tested purity and has been dried for 2 hours at 100° C.) in a liter of water. Place 50 cc. of the standard solution, containing 0.5 gram of Br, in a glass-stoppered flask having a capacity of about 200 cc. Acidify this with 10 cc. of dil. H_2SO_4 (1:4), shake the whole and let stand a few minutes. Then let the wood alcohol flow slowly into the mixture, drop by drop, from a burette until the color is entirely discharged. The rate of flow from the burette shall not exceed 5 cc. per minute. The temperature of the mixture should be 20° C.

In addition to the above requirements the methyl alcohol must be of such a character as to render the ethyl alcohol with which it is mixed unfit for use as a beverage.

REFERENCE.—*Regulations* No. 61 Revised, U. S. Internal Revenue (1925). (See also Treasury Decision 2779.)

GRAIN ALCOHOL OR COLOGNE SPIRITS

General.—The sample should be clear and colorless and have the characteristic odor of ethyl alcohol. Medicinal alcohol should pass all the qualitative tests of the U. S. Pharmacopœia.

Specific Gravity.—Determine the sp. gr. at 60° F. with a Westphal balance or with a pycnometer. The temperature must be exactly 60° F. (15.56° C.).

Ethyl Alcohol.—Calculate the percentage of ethyl alcohol both by volume and by weight from the sp. gr. The tables for these calculations will be found in Leach's "Food Inspection and Analysis" (4th edition), pages 690–703; also in Van Nostrand's "Chemical Annual."

Proof.—To obtain the proof multiply by 2 the percentage of ethyl alcohol *by volume.*

Non-volatile Residue.—Evaporate 100 cc. in a weighed platinum dish nearly to dryness on the water bath, then transfer to a water oven and dry at the temperature of boiling water for 2.5 hours. Cool in a desiccator and weigh. To obtain the percentage of non-volatile residue divide the weight obtained by the sp. gr. of the sample.

Acidity, Calculated as Acetic Acid.—Titrate 100 cc. of the sample with 0.1 N NaOH and phenolphthalein, until a permanent pink color is formed.

CALCULATION.—1 cc. 0.1 N NaOH = 0.0060 gram acetic acid.

Esters.—Dilute 250 cc. of the sample with 30 cc. of water and distill slowly into a 250-cc. volumetric flask until nearly filled to the mark. Make up to volume with water. Shake and mix thoroughly and use aliquot portions of this solution (*solution A*) for the determination of esters, aldehydes and furfural.

Pipette 50 cc. of solution *A* into a 300-cc. Erlenmeyer flask and exactly neutralize with 0.1 N NaOH and phenolphthalein. Then add 25–50 cc. excess of the 0.1 N NaOH, accurately measured. Either boil for 1 hour with a reflux condenser or let stand overnight in the stoppered flask and heat with a reflux condenser for one-half hour below the boiling point. Cool, and titrate with 0.1 N acid and phenolphthalein. Multiply the number of cc. of

0.1 N NaOH consumed in the saponification by 0.0088. The result is the weight in grams of the esters calculated as ethyl acetate. Divide this weight by the sp. gr. of the sample and multiply by 2 to obtain the percentage.

Aldehydes (Qualitative $AgNO_3$ Test.)—Make up a solution of the following: 3 grams of $AgNO_3$, 3 grams of NaOH and 20 cc. of conc. NH_4OH. Dissolve the $AgNO_3$ in a little water in a 100-cc. volumetric flask, add the NH_4OH and then the NaOH and then make up to 100 cc. Dilute 10 cc. of the sample with 10 cc. of water and place in a glass-stoppered bottle, adding 1 cc. of the above alkaline $AgNO_3$ solution. Let stand for 1 hour in the dark and filter immediately. Test the filtrate for Ag by adding an excess of HNO_3 and then a few drops of HCl. If this produces a precipitate of AgCl (showing unreduced Ag salts), the alcohol contains less than the maximum allowable amount of aldehyde.

NOTE.—This test is from Government specification, January 20, 1907.

Aldehydes (Quantitative Determination).—SOLUTIONS REQUIRED—(*a*) *Alcohol Free from Aldehydes.*—Place 1500 cc. of ordinary 95% alcohol in a 2-liter distilling flask, add about 25 grams of NaOH (or KOH) and distill down to about 100 cc. Add to the distillate 2.5 grams of meta-phenylenediamine hydrochloride, stopper and let stand for several days (or place on the steam bath in a large flask and reflux for several hours). Then distill slowly, rejecting the first 100 cc. and the last 200 cc.

(*b*) *Sulfite-Fuchsin Solution.*—Dissolve 0.50 gram of pure fuchsin in 500 cc. of water, then add 5 grams of SO_2 dissolved in water.* Make up to a liter and let stand until colorless. Prepare the solution in small quantities and keep at a low temperature, as it retains its strength for only a few days.

(*c*) *Standard Acetaldehyde Solution.*—Grind about 5 grams of aldehyde ammonia in a mortar with ether and decant the ether. Repeat this operation several times, then dry the purified salt in a current of air and finally in a vacuum desiccator over conc. H_2SO_4. Dissolve 1.386 grams of this purified aldehyde ammonia in 50 cc. of 95% alcohol, add 22.7 cc. of N alcoholic H_2SO_4 (a solution of 95% alcohol containing 49.04 grams of H_2SO_4 per

* Saturate a liter of distilled water with SO_2 gas. Titrate an aliquot with 0.1 N iodine and calculate the amount of SO_2 in 1 cc. of the solution. Then measure out a sufficient number of cc. to contain 5 grams of SO_2.

liter), make up to 100 cc. with 95% alcohol and add 0.8 cc. extra to compensate for the volume of $(NH_4)_2SO_4$ precipitated. Let the mixture stand overnight and filter. This solution contains 1 gram of acetaldehyde in 100 cc. and will retain its strength.

The standard found most convenient for use is 2 cc. of this strong aldehyde solution diluted to 100 cc. with 50% alcohol (by volume). One cc. of this solution = 0.0002 gram of acetaldehyde. This solution should be made up fresh, as it loses its strength in a a day or two.

PROCEDURE.—Determine the aldehyde in solution *A* as follows:

Dilute 10 cc. to 50 cc. with aldehyde-free alcohol (50% by volume). Add 25 cc. of the fuchsin solution and let stand 15 minutes at 15° C. The solutions and the reagents should all be at 15° C. when they are mixed. Prepare standards of known strength from the standard acetaldehyde solution in the same way and match them colorimetrically with the sample. Calculate the percentage of aldehydes in the original sample (10 cc. of solution *A* = 10 cc. of the original sample).

Furfural.—Dilute 20 cc. of solution *A* to 50 cc. with furfural-free alcohol (50% by volume). Add 2 cc. of colorless aniline and 0.5 cc. of dil. HCl (5 : 4) and keep for 15 minutes in a water bath at about 15° C. Prepare standards of known strength from the standard furfural solution and blanks in the same way and match up the colors. Calculate the weight of furfural in the original sample. The comparison standards found most convenient for use contain from 0.00005 to 0.00030 gram of furfural, in increments of 0.00005 gram.

Standard Furfural Solution.—Dissolve 1 gram of freshly redistilled furfural in 100 cc. of 95% alcohol. This strong solution will keep. Make fresh standards by diluting 1 cc. to 100 cc. with 50% alcohol (by volume). 1 cc. of this weak solution contains 0.0001 gram of furfural.

Fusel Oil.—To 100 cc. of the original sample in a 300-cc. Erlenmeyer flask add 20 cc. of 0.5 N NaOH and saponify the mixture by boiling for 1 hour under a reflux condenser. (The same result will be obtained by letting the mixture stand at room temperature overnight.) Connect the flask to a condenser and distill over 90 cc., then add 25 cc. of water to the flask and continue the distillation until a total of 115 cc. has been collected.

Whenever aldehydes are present in excess of 15 parts per 100,000, add to the distillate 0.5 gram of metaphenylenediamine hydrochloride, boil under a reflux condenser for 1 hour, distill 100 cc., add 25 cc. of water, and continue the distillation until an additional 25 cc. are collected.

Nearly saturate the distillate with finely ground salt (NaCl) and add a saturated solution of salt until the sp. gr. is 1.10. Extract this salt solution four times with purified CCl_4,* using 40, 30, 20, and 10 cc., respectively, and wash the CCl_4 three times with 50-cc. portions of saturated NaCl solution and twice with saturated Na_2SO_4 solution. Transfer the CCl_4 to a flask containing 50 cc. of oxidizing solution (made by dissolving 100 grams of $K_2Cr_2O_7$ in 900 cc. of water and adding 100 cc. of conc. H_2SO_4) and boil for 8 hours under a reflux condenser. Add 30 cc. of water and distill until only about 20 cc. remain. Neutralize the distillate to methyl orange and titrate the valeric acid formed by oxidation of the amyl alcohol with 0.1 N NaOH, using phenolphthalein indicator. Calculate the titration to amyl alcohol (fusel oil).

CALCULATION.—1 cc. 0.1 N NaOH = 0.0088 gram amyl alcohol.

NOTES.—(1) If the distillations have been conducted properly, the distillate will not show a marked acid reaction to methyl orange. Should much more than 1 cc. of 0.1 N NaOH be required for neutralization, the result will be unreliable and the determination should be repeated. A blank determination should also be conducted upon 100 cc. of the CCl_4, beginning the blank just before the washings of the CCl_4 with NaCl and Na_2SO_4 solutions.

(2) Rubber stoppers may be used in the saponification and first distillation, but corks covered with tinfoil must be used in the oxidation and second distillation. Renew the corks and tinfoil frequently.

Methyl Alcohol (Wood Spirit). (*A*) RICHE AND BARDY METHOD.—This method for the detection of methyl alcohol in commercial spirit of wine depends on the formation of methylaniline violet. The procedure is described on page 657.

(*B*) OXIDATION METHOD.—Dilute 20 cc. of the sample to 100 cc. and place in a 200-cc. distilling flask. Add 5–8 grams of

* Mix ordinary CCl_4 with one-tenth its volume of conc. H_2SO_4, shake thoroughly at frequent intervals and let stand overnight. Wash free from acid and impurities with tap water. Remove the water, add an excess of NaOH solution and distill the CCl_4.

chromic acid (CrO_3) to oxidize the methyl alcohol to formaldehyde. Distill, collect 10 cc. of the distillate, and test for formaldehyde by one of the following methods:

(1) *Hehner's Method.*—To the distillate obtained above add 100 cc. of fresh milk and mix. Fill a test-tube about one-third full of the mixture and pour conc. H_2SO_4 carefully down the side, not allowing the two to mix. A violet or blue color at the junction of the two liquids indicates formaldehyde. This test is sensitive to about 1 part in 10,000 of the liquid tested.

(2) *Leach's Method.*—Mix the distillate above described with an equal volume of pure milk in a porcelain casserole and add about 10 cc. of conc. HCl containing about 1 cc. of 10% $FeCl_3$ solution to each 500 cc. of acid. Heat to 80–90° C. directly over the gas flame, giving the casserole a rotary motion to break up clots. A violet color indicates formaldehyde.

(3) *Morphine Sulfate Test.*—Dissolve 0.5 gram of morphine sulfate in 500 cc. of conc. H_2SO_4. Place about 5 cc. of this solution in a test-tube and add 1–2 cc. of the distillate above referred to. A violet color on standing shows formaldehyde.

NOTE.—A blank test should always be carried out simultaneously with pure ethyl alcohol and with ethyl alcohol to which is added a little methyl alcohol.

Nitrates.—Neutralize 50 cc. of the sample with 0.1 N NaOH (phenolphthalein) and evaporate nearly to dryness. Take up with a little distilled water and add 1 cc. of phenoldisulfonic acid; then make alkaline with NH_4OH. A bright orange-yellow color indicates the presence of nitrates. A blank should be run at the same time, evaporating 50 cc. of distilled water to make sure that no nitrate fumes have been picked up during the evaporation.

Sulfur Compounds.—Place 100 cc. of the sample in a platinum dish and make slightly alkaline with 0.1 N NaOH (phenolphthalein). Add 5 cc. of H_2O_2, evaporate to dryness and ignite over an alcohol lamp. Dissolve the residue in 50 cc. of water, add 5 cc. of dil. HCl, bring to boiling and add 5 cc. of 10% $BaCl_2$ solution. If any precipitate forms after boiling for 15 minutes, filter it out, ignite and weigh in the usual manner. Calculate to sulfur.

CALCULATION.—$BaSO_4 \times 0.1373 = S$.

NOTE.—A blank should be run at the same time, using the same amounts of each reagent as used in the determination. If the blank shows any sulfur, its amount should be determined and subtracted from the weight previously found.

REFERENCES.—*U. S. Dept. Agr.*, Bureau of Chem., *Cir.* 74, p. 5; *U. S. Dept. of Agr.*, Bureau of Chem., *Bull.* 107, revised, p. 185; Leach: "Food Inspection and Analysis," 4th ed., 777; *U. S. Pharmacopœia*, 9th ed., 35; Association of Official Agricultural Chemists: "Methods of Analysis," 369–373 (1925).

FORMALDEHYDE SOLUTION

General.—Formaldehyde is a gaseous substance of the formula HCHO. It is used in aqueous solution as a disinfectant, insecticide and deodorizer. The U. S. P. solution should contain not less than 37% by weight of HCHO. The solution also generally contains more or less methyl alcohol to prevent polymerization.

The following procedures for the determination of formaldehyde are recognized as official methods by the Association of Official Agricultural Chemists.

Hydrogen Peroxide Method. REAGENTS.—(*a*) *Normal* H_2SO_4.

(*b*) *Normal NaOH* (1 cc. = 0.03002 gram HCHO).

(*c*) *Hydrogen Peroxide:* An approximately 3% solution. If the solution is acid, neutralize with (*b*), using litmus solution as indicator.

(*d*) *Litmus Solution:* A solution of purified litmus of sufficient strength so that 3 drops will impart a distinct blue color to 50 cc. of water.

DETERMINATION.—Measure 50 cc. of N NaOH into a 500-cc. Erlenmeyer flask and add 50 cc. of the H_2O_2. Then add from a weighing pipette 3 cc. of the sample, letting the point of the pipette reach nearly to the liquid in the flask. Place a funnel in the neck of the flask and heat on the steam bath for 5 minutes, shaking occasionally. Remove from the steam bath, wash the funnel with water, cool the flask to about room temperature, and titrate the excess of NaOH with N acid, using litmus solution as indicator. It is necessary to cool the flask before titration with the acid to get a sharp end-point. Calculate the percentage of formaldehyde from the amount of normal NaOH consumed.

NOTE.—The *U. S. Pharmacopœia* requires that formaldehyde solution shall not contain sufficient free acid to neutralize more than 1 cc. of N NaOH solution when 20 cc. of the liquid are titrated, using phenolphthalein indica-

tor. For accurate results in the HCHO determination by the above method the amount of N NaOH consumed should be corrected for the amount neutralized by the acidity. If the acidity is excessive, it should also be calculated and reported in terms of formic acid.

1 cc. 1.0 N NaOH = 0.046 gram HCO_2H.

Cyanide Method.*—Reagents.—(*a*) *0.1 N* $AgNO_3$.

(*b*) *0.1 N* NH_4SCN.

(*c*) *KCN solution:* Dissolve 3.1 grams of KCN in 500 cc. of water.

(*d*) *50%* HNO_3.

Determination.—Treat 15 cc. of 0.1 N $AgNO_3$ with 6 drops of 50% HNO_3 in a 50-cc. volumetric flask. Add 10 cc. of KCN solution. Dilute to volume; shake well; filter through a dry filter, and titrate 25 cc. of the filtrate with 0.1 N NH_4SCN, using 5 cc. of a saturated solution of ferric alum as indicator, and continue the titration until the first appearance of a permanent light-brown color. Acidify another 15-cc. portion of 0.1 N $AgNO_3$ with 6 drops of 50% HNO_3 and treat with 10 cc. of the KCN solution to which has been added a measured quantity (the weight of which must be calculated from the sp. gr.) of the formaldehyde solution, containing not over 0.025 gram of HCHO. Make up to 50 cc., filter and titrate a 25-cc. aliquot with 0.1 N NH_4SCN for the excess of Ag as before. The difference between the number of cc. of 0.1 N sulfocyanate used in these two titrations, multiplied by 2, gives the number of cc. of 0.1 N sulfocyanate corresponding to the KCN consumed by the formaldehyde. Calculate the percentage of formaldehyde present.

Calculation.—1 cc. 0.1 N sulfocyanate = 0.003002 gram HCHO.

Reference.—Association of Official Agricultural Chemists: "Methods of Analysis," 67 (1925).

FORMIC ACID

General.—Formic acid occurs in solutions of varying strengths, such as 30, 50, 75 and 90%. The weaker solutions are generally made by diluting the stronger. There are also often present HCl and H_2SO_4, the amount depending upon the extent to which the material has been purified.

* Applicable only to dilute solutions.

Specific Gravity at 15.5° C.—This may be determined by the Westphal balance; if great accuracy is desired, a pycnometer should be used.

Sulfuric Acid.—Weigh approximately 20 grams from a weighing bottle into a beaker. Dilute with 250 cc. of water; add 5 cc. of conc. HCl; heat to boiling, and add an excess of hot 10% $BaCl_2$ solution. Continue the boiling for at least 15 minutes. Let stand several hours. Filter out the $BaSO_4$, wash, ignite, and weigh in the usual manner. Calculate to H_2SO_4.

CALCULATION.—$BaSO_4 \times 0.4202 = H_2SO_4$.

Hydrochloric Acid.—Weigh 10–20 grams of the liquid into a 300-cc. Erlenmeyer flask. (This flask should previously have been cleaned with sulfuric acid bichromate solution, to remove all the grease and prevent sticking of the precipitate.) Dilute with 150 cc. of water; add 5 cc. of conc. HNO_3 and then $AgNO_3$ solution in excess. Shake the liquid in the flask until the precipitate settles clearly. Filter through a weighed Gooch crucible, washing with cold distilled water. Dry the precipitate in the crucible at 100–110° C., then place the Gooch crucible in a large platinum crucible and ignite gently until the edges of the precipitate just *begin* to fuse. Cool in a desiccator and weigh the AgCl. Calculate to HCl.

CALCULATION.—$AgCl \times 0.2544 = HCl$.

Formic Acid.—Weigh 8–10 grams accurately from a weighing bottle into a 500-cc. volumetric flask about one-half full of distilled water. Make up to the mark and mix thoroughly. Pipette 50 cc. of this solution into a 300-cc. Erlenmeyer flask. Make the solution alkaline with Na_2CO_3 solution. Warm and add a measured excess of standard 0.1 N $KMnO_4$. It is very necessary that an *excess* of the permanganate be added. This oxidizes the formic acid to CO_2 and water and throws down a heavy precipitate of MnO_2. Then acidify with 10 cc. of dil. H_2SO_4. Run in from a burette a measured volume of 0.1 N oxalic acid* until all the precipitate has dissolved and all the permanganate color has disappeared. Finally titrate the excess of $H_2C_2O_4$ with the 0.1 N $KMnO_4$. The difference between the total 0.1 N $KMnO_4$ used

* It is not absolutely necessary to have the oxalic acid of a definite strength. In case, however, it is not 0.1 N, measure off a volume of the oxalic acid equal to that used in the determination and titrate it against the 0.1 N $KMnO_4$.

and the amount which was equivalent to the $H_2C_2O_4$ gives the number of cc. of 0.1 N $KMnO_4$ required to oxidize the formic acid.

CALCULATION.—1 cc. 0.1 N $KMnO_4$ = 0.002301 gram formic acid.

NOTE.—If other acids are known to be absent, the amount of formic acid can be determined by titrating directly with 0.1 N NaOH and phenolphthalein.

1 cc. 0.1 N NaOH = 0.004602 gram formic acid.

REFERENCE.—*Am. Chem. Jour.*, **17,** 539 (1895).

ACETIC ANHYDRIDE

General.—Acetic anhydride is a very corrosive substance and its vapors are extremely irritating to the eyes and lungs. Care should therefore be exercised in working with it, and any spilled upon the hands should be immediately washed off. It is a condensation of 2 molecules of acetic acid with elimination of water. The reaction, however, is reversible, and there is always present some acetic acid, due to action of water, thus:

$$(CH_3CO)_2O + H_2O \rightleftarrows 2CH_3COOH.$$

Determination of Anhydride Content.—When the material is pure and contains only acetic anhydride and acetic acid, the direct titration method, described below, gives satisfactory results. In case of impure samples, however, the aniline method should be employed. The latter method is the one employed by the U. S. Government and should always be used unless otherwise expressly directed.

DIRECT TITRATION.—Weigh accurately about 25 grams from a weighing bottle into a 2-liter volumetric flask, partly filled with CO_2-free water; let stand overnight, make up to volume with CO_2-free water and titrate 50-cc. aliquots with 0.1 N NaOH and phenolphthalein. Calculate the titration to acetic acid.

1 cc. 0.1 N NaOH = 0.006003 gram acetic acid.

Since 100% of acetic anhydride is equivalent to 117.654% of acetic acid, then

$$\text{percentage of acetic anhydride} = \frac{A - 100}{117.654 - 100} \times 100$$

$$= 5.664(A - 100),$$

where A is the percentage of acetic acid found by titration.

NOTE.—As any error in the acetic acid result is increased nearly sixfold in the final results, the titration should be carried out with great care and the average of several aliquots should be taken. Corrections for burette calibrations must be made and also corrections for temperature effects on the standard solution. The standard NaOH should be as free from carbonate as possible.

ANILINE METHOD.—Shake the sample thoroughly and rinse a burette twice with portions of it. Clean and dry two 50-cc. weighing bottles, and two of 5-cc. size. (Do not use alcohol for drying the weighing bottles or any of the apparatus used in weighing out the anhydride.)

Into each of the 5-cc. weighing bottles, which have been carefully weighed, run 2 cc. of anhydride from the burette. Immediately stopper the bottles and weigh again to obtain the weight of anhydride. Then drop very carefully each weighing bottle with its contents into a separate 300-cc. Erylenmeyer flask containing 50 cc. of N NaOH and 50 cc. of water. Loosen the stopper of the weighing bottle slightly before dropping it into the flask, so that it can be freed from the weighing bottle and the contents mixed with the NaOH solution. Let the mixture stand 30–45 minutes at room temperature with occasional shaking. Then titrate with N or 0.5 N acid and phenolphthalein. Add 2 or 3 cc. of acid in excess and let the solution stand about 15 minutes longer with occasional shaking. Finally titrate back the excess of acid with 0.1 N NaOH to the first permanent pink color. From this titration calculate the number of cc. of N NaOH representing the total acetic acid from 100 grams of the sample. Call this *A*.

Into each of the 50-cc. weighing bottles run about 20 cc. of perfectly dry and recently distilled aniline. (The aniline should be distilled over solid NaOH, discarding the first portion of distillate.) Then add 2 cc. of anhydride from the burette. This operation requires considerable care. Do not add the anhydride too rapidly, and distribute it through the aniline as thoroughly as possible by keeping the aniline swirling slightly in the weighing bottle during the addition. When the anhydride has been added, stopper the bottle and set aside to come to room temperature; then weigh to obtain the weight of anhydride added.

At the end of about 1 hour from the time of addition of the anhydride to the aniline, transfer the mixture to a 500-cc. volu-

metric flask and make up to the mark with a solution of equal parts of neutral alcohol and water. Titrate 50 cc. of this solution with 0.1 N NaOH. From this titration calculate the number of cc. of N NaOH corresponding to the residual acetic acid from 100 grams of the sample. Call this *B*.

Subtract *B* from *A* to obtain the number of cc. of N NaOH corresponding to one-half the anhydride in 100 grams of sample. This value multiplied by 0.10205* gives grams of acetic anhydride per 100 grams of sample, *i.e.*, the percentage.

Mineral Acids.—Shake up a portion of the sample with cold water and test the solution in the usual way for HCl with $AgNO_3$ and for H_2SO_4 with $BaCl_2$. The determination may be made quantitative by starting with a weighed amount of the anhydride sample.

NOTE.—If mineral acids are found present, corrections must be made for the amount of NaOH they will neutralize in making the anhydride titration.

Boiling Point.—The boiling point of pure acetic anhydride is approximately 138° C. and a satisfactory sample should all distill between 130 and 140° C.

REFERENCE.—Worden: "Technology of Cellulose Esters," **8**, 2910–2917.

GLYCEROL

General.—There are two recognized methods for the determination of glycerol—(1) the acetin method, which depends upon the conversion of glycerol into triacetin with sodium acetate and acetic anhydride and a quantitative saponification of the triacetin thus formed; (2) the bichromate method, which is based on the fact that $K_2Cr_2O_7$ in the presence of H_2SO_4 completely oxidizes glycerol to CO_2 and H_2O.

The acetin method is the one agreed upon at a conference of delegates from the British, French, German, and American committees on glycerol analysis as giving results nearer to the truth than the bichromate method on crude glycerines in general. It is the method to be employed whenever possible, but *for the*

* It will be noted that the factor is the molecular weight of acetic anhydride divided by 1000. The method may be applied to other anhydrides, *e.g.*, butyric anhydride (Mol. Wt. = 158.11), in which case the factor will be 0.001 of the molecular weight of the anhydride in question.

application of this method the solution must not contain over 60% of water. In general, therefore, use the acetin method for crude or refined glycerines and the bichromate method for soap lyes.

Acetin Method

Reagents Required.—(*a*) *Best Acetic Anhydride.*—This should be carefully selected. A good sample must not require more than 0.1 cc. of N NaOH for saponification of the impurities when a blank is run on 7.5 cc. Only a slight color should develop during digestion of the blank. (See under Blank Test below.)

The anhydride may be tested for strength by the aniline method described under analysis of Acetic Anhydride (page 106).

(*b*) *Pure Fused Sodium Acetate.*—Re-fuse the ordinary salt in a platinum, silica, or nickel dish, avoiding charring; powder quickly and keep in a stoppered bottle or desiccator. It is very important that the sodium acetate be anhydrous.

(*c*) *NaOH* (*Approximately N and Free from Carbonate*).—Dissolve pure NaOH in its own weight of water (free from CO_2). Let settle till clear or filter through asbestos. Dilute the clear solution with water free from CO_2 to the strength required.

(*d*) *N NaOH* (*Free from Carbonate*).—Prepare this solution as above but carefully standardize it. Some NaOH solutions show a marked diminution in strength after boiling; such solutions should be rejected.

(*e*) *N Acid.*—Standardize this against the N NaOH.

(*f*) *Phenolphthalein Solution.*—Dissolve the powder in alcohol sufficient to make a 0.5% solution and neutralize with N NaOH to a very slight pink color.

Procedure.—In a narrow-mouthed flask (preferably round-bottomed), capacity about 120 cc., which has been thoroughly cleaned and dried, weigh accurately and as rapidly as possible 1.25–1.50 grams of the glycerine. A Grethun or Lunge pipette will be found convenient. Add about 3 grams of anhydrous sodium acetate and 7.5 cc. of acetic anhydride, and connect the flask with an upright Liebig condenser. For convenience the inner tube of this condenser should not be over 50 cm. long and 9–10 mm. inside diameter. The flask is connected to the condenser by either a ground-glass joint (preferably) or a rubber

stopper. If a rubber stopper is used, it should have had a preliminary treatment with hot acetic anhydride vapor.

Heat the contents and keep just boiling for 1 hour, taking precautions to prevent the salts from drying on the sides of the flask. Let the flask cool somewhat, and through the condenser tube add 50 cc. of water, free from CO_2, at a temperature of about 80° C., taking care that the flask is not loosened from the condenser. The object of cooling is to avoid any sudden rush of vapors from the flask on adding water, and to avoid breaking the flask. Time is saved by adding the water before the contents of the flask solidify, but the contents may be allowed to solidify and the test proceeded with the next day without detriment, bearing in mind that the anhydride in excess is much more effectively hydrolyzed in hot than in cold water. The contents of the flask may be warmed to, but must not exceed, 80° C. until solution is complete except for a few dark flocks representing organic impurities in the crude glycerine. By giving the flask a rotary motion, solution is more quickly effected.

Cool the flask and contents without removing the condenser. When quite cold, wash down the inside of the condenser tube, detach the flask, wash off the stopper or ground-glass connection into the flask, and filter the contents through an acid-washed filter into a Pyrex glass flask of about 1-liter capacity. Wash thoroughly with cold distilled water free from CO_2. Add 2 cc. of phenolphthalein solution (*f*), then run in NaOH solution (*c*) or (*d*) until a faint pinkish yellow color appears throughout the solution. This neutralization must be done most carefully; the alkali should be run down the sides of the flask, the contents of which are kept rapidly swirling with occasional agitation or change of motion until the solution is nearly neutralized, as indicated by the slower disappearance of the color developed locally by the alkali running into the mixture. When this point is reached the sides of the flask are washed down with CO_2-free water and the alkali subsequently added drop by drop, mixing after each drop until the desired tint is obtained.

Now run in from a burette 50 cc. or a calculated excess of N NaOH (*d*) and note carefully the exact amount. Boil gently for 15 minutes, the flask being fitted with a glass tube acting as a partial condenser. Cool as quickly as possible and titrate

the excess of NaOH with N acid (*e*) until the pinkish yellow or chosen end-point color just remains.* A further addition of the indicator at this point will cause an increase of the pink color; this must be neglected, and the first end-point taken.

From the N NaOH consumed calculate the percentage of glycerol (including acetylizable impurities) after making the correction for the blank test described below.

1 cc. N NaOH = 0.03069 gram glycerol.

The coefficient of expansion for normal solutions is 0.00033 per cc. for each degree Centigrade. A correction should be made on this account if necessary.

Blank Test.—As the acetic anhydride and sodium acetate may contain impurities which affect the result, it is necessary to make a blank test, using the same quantities of acetic anhydride, sodium acetate and water as in the analysis. It is not necessary to filter the solution of the melt in this case, but sufficient time must be allowed for the hydrolysis of the anhydride before proceeding with the neutralization. After neutralization it is not necessary to add more than 10 cc. of the N alkali (*d*), as this represents the excess usually present after the saponification of the average soap lye crude. In determining the acid equivalent to the N NaOH, however, the entire amount taken in the analysis, 50 cc., should be titrated after dilution with 300 cc. of water free from CO_2 and without boiling.

Glycerol Value of Acetylizable Impurities.—Certain crude glycerines may contain a considerable amount of acetylizable impurities other than glycerol. To determine the amount of these impurities, dissolve the *total residue at 160° C.* (see below) in 1 or 2 cc. of water, wash into the acetylizing flask and evaporate to dryness. Then add anhydrous sodium acetate and acetic anhydride in the usual amounts and proceed as described in the regular analysis.

True Glycerol Content.—After correcting for the blank calculate the result obtained in the preceding paragraph to glycerol and subtract the amount from the total amount of glycerol obtained in the analysis.

* A precipitate at this point is an indication of the presence of iron or alumina, and high results will be obtained unless a correction is made as described below.

Total Residue at 160° C.—If the glycerine is acid, make it slightly alkaline with Na_2CO_3 to prevent the loss of organic acids. To avoid the formation of polyglycerols this alkalinity must not exceed 0.2% Na_2O. If, therefore, the glycerine is too strongly alkaline, sufficient N HCl must be added to bring the alkalinity down to 0.2%.

Place 10 grams of the sample in a 100-cc. flask, dilute with water and add the calculated quantity of N HCl or Na_2CO_3 to give the required degree of alkalinity. Dilute to 100 cc., mix thoroughly and pipette 10 cc. into a weighed Petri or similar dish, 2.5 inches in diameter and 0.5 inch deep, with a flat bottom. In the case of crude glycerines abnormally high in organic residue, a smaller amount should be taken so that the amount of the organic residue does not materially exceed 30–40 milligrams.

Place the dish on a water bath until most of the water is evaporated, then place in an oven and evaporate the glycerine, or most of it at least, at a temperature of 130–140° C. When only a slight vapor is seen to come off, take out the dish and let it cool. Add 0.5–1 cc. of water and bring the residue wholly or nearly into solution with a rotary motion. Place the dish on the water bath or on top of the oven until the excess water has evaporated and the residue is in such a condition that it will not spurt if the oven is raised to 160° C. In the meantime set the oven at exactly 160° C. From this point the time of heating must be strictly observed. Place the dish in the oven and maintain at exactly 160° C. for 1 hour. Remove the dish, cool, treat the residue with water, and evaporate the water as before. Then place the dish again in the oven and heat a second time for exactly 1 hour. Place the dish in a desiccator and let cool over conc. H_2SO_4. Weigh the cooled dish. Again moisten with water and heat at 160° C. for 1 hour. Repeat the operation until a constant loss of 1–1.5 mg. per hour is obtained.

In the case of acid glycerine correct for the N Na_2CO_3 added by subtracting 0.03 gram for each cc. added. In the case of alkaline glycerine correct for the amount of N HCl added by calculating the increase in weight due to the conversion of the NaOH and Na_2CO_3 to NaCl. From the corrected weight calculate the percentage of total residue at 160° C. This residue is

taken for the determination of the *non-volatile acetylizable impurities* (see above).

Bichromate Method

Reagents Required.—(*a*) *Pure* $K_2Cr_2O_7$, powdered and dried at 110–120° C. in air free from dust or organic vapors. This is taken as the standard.

(*b*) *Dilute Bichromate Solution.*—Dissolve 7.4564 grams of the above bichromate in distilled water and make up the solution to 1 liter at 15.5° C.

(*c*) *Ferrous Ammonium Sulfate Crystals.*—It is never safe to assume this salt to be constant in composition, and the solution must be standardized against the bichromate as follows:

Dissolve 3.7282 grams of bichromate (*a*) in 50 cc. of water. Add 50 cc. of 50% H_2SO_4 (by volume), and to the cold undiluted solution add from a weighing bottle a moderate excess of the ferrous ammonium sulfate, and titrate back with the dilute bichromate (*b*). Calculate the value of the ferrous salt in terms of bichromate.

(*d*) *Silver Carbonate.*—Prepare this as required for each test. Make up a 0.5% Ag_2SO_4 solution and precipitate the Ag_2CO_3 from 140 cc. of this solution with about 4.9 cc. of N Na_2CO_3 solution. (A little less than the calculated quantity of N Na_2CO_3 should be used as an excess prevents rapid settling.) Let settle, pour off the liquid and wash once by decantation.

(*e*) *Subacetate of Lead.*—Boil a 10% solution of pure lead acetate with an excess of litharge (PbO) for 1 hour, keeping the volume constant, and filter while hot. Disregard any precipitate which subsequently forms. Preserve out of contact with CO_2.

(*f*) *Potassium Ferricyanide.*—Use a freshly prepared, very dilute solution of this salt, containing about 0.1%.

Procedure.—Weigh out 20 grams of the glycerine, make up with water to 250 cc. in a volumetric flask and pipette out 25 cc. into a 100-cc. volumetric flask. To this add the Ag_2CO_3, let stand with occasional agitation for about 10 minutes, and add a slight excess (about 5 cc. in most cases) of basic lead acetate (*e*). Let stand a few minutes, dilute with water to 100 cc. and then add 0.15 cc. to compensate for the volume of the precipitate. Mix thoroughly, filter through an air-dry filter into a test-tube.

rejecting the first 10 cc., and return the filtrate, if not clear and bright. Test a portion of the filtrate with a little basic lead acetate, which should produce no further precipitate. In the great majority of cases 5 cc. are ample, but occasionally a crude will be found requiring more, and in this case another aliquot of 25 cc. of the dilute glycerine should be purified with 6 cc. of basic lead acetate. Care must be taken to avoid a marked excess of basic acetate.

When the filtrate is coming through perfectly clear, collect sufficient in an Erlenmeyer flask so that 25 cc. may be pipetted into a flask or beaker which has been previously cleaned with $K_2Cr_2O_7$ and H_2SO_4. To this add 12 drops of dil. H_2SO_4 (1:4) to precipitate the small excess of lead as $PbSO_4$. Then add 3.7282 grams of the powdered $K_2Cr_2O_7$. Rinse down the bichromate with 25 cc. of water and let stand with occasional shaking until all the bichromate is dissolved. (No reduction will take place in the cold.)

Add 50 cc. of dil. H_2SO_4 (1 : 1), immerse the vessel in boiling water for 2 hours and keep protected from dust and organic vapors, such as alcohol, until the titration is completed. Add from a weighing bottle a slight excess of the ferrous ammonium sulfate, making spot tests on a porcelain plate with ferricyanide indicator until an excess is shown by a blue color. Then titrate back with the dilute bichromate solution. Calculate the percentage of glycerol from the amount of bichromate reduced.

CALCULATION.—1 gram $K_2Cr_2O_7 = 0.13411$ gram glycerol.

NOTES.—(1) The percentage of glycerol obtained above includes any oxidizable impurities present after the purification. A correction for the non-volatile impurities may be made by running a bichromate test on the Residue at 160° C.

(2) It is important that the concentration of acid in the oxidation mixture and the time of oxidation should be strictly adhered to.

(3) Before the bichromate is added to the glycerine solution it is essential that the slight excess of lead be precipitated with H_2SO_4, as stipulated.

(4) For crudes practically free from chlorides the quantity of Ag_2CO_3 may be reduced to one-fifth and the basic lead acetate to 0.5 cc.

(5) It is sometimes advisable to add a little K_2SO_4 to insure a clear filtrate.

(6) Neither the acetin nor the bichromate method is correct in theory or in practice on crudes containing trimethyleneglycol or polyglycerols but the acetin method gives nearer the truth.

REFERENCE.—*J. Ind. Eng. Chem.*, **3**, 679 (1911). Approved Report of the Subcommittee on Glycerine Analysis.

DEXTRIN OR BRITISH GUM

General.—Dextrin corresponds to the chemical formula $(C_6H_{10}O_5)_n$ and is generally considered an intermediate product between starch and dextrose. The commercial product is made by heating dry starch to 200–250° C. or by moistening the starch with acid, drying at 50° C. and then heating to 140–170° C. The product is an indefinite mixture of several dextrins with unchanged starch and may also contain more or less dextrose. The dextrins are soluble in cold water and form a thick, viscous syrup which has strong adhesive properties and is much used as a substitute for gum arabic in the preparation of mucilage and for thickening color in calico printing, etc.

Moisture.—Dry 5 grams to constant weight at 100° C. in a weighed platinum dish.

Ash.—Ignite carefully the residue from the moisture determination to a white or grayish white ash. Cool in a desiccator and weigh.

Insoluble in Cold Water (Starch).—Stir into about 250 cc. of water 25 grams of the sample. Wash into a 500-cc. volumetric flask. Shake occasionally for several hours, dilute to volume and let stand overnight. Pipette out 50 cc. of the clear supernatant liquor, evaporate in a weighed dish on the water bath and dry to constant weight at 100° C. This gives the weight of the soluble solids in 2.5 grams. Divide by 2.5 and multiply by 100 to obtain the percentage of soluble solids. Add to this the percentage of moisture and subtract the sum from 100%. The difference is insoluble matter (unconverted starch).

Dextrose. (Munson and Walker Method.)—Mix 10 grams of the sample with water, stir thoroughly and wash into a 250-cc. volumetric flask. Add 5 cc. of lead subacetate solution, dilute to volume, mix thoroughly, let settle and filter through a dry filter. Do not wash. Add a few crystals of anhydrous $K_2C_2O_4$ to remove the lead and again filter through a dry filter. Pipette out 50 cc. of this solution and determine reducing sugars according to the Munson and Walker method described on page 551.

Calculate to dextrose, using the third column of figures in the Munson and Walker tables.

Dextrin.—Pipette 100 cc. of the solution of the material prepared for the dextrose determination (after the Pb has been removed and the solution filtered), into a 250-cc. flask, and add 20 cc. of dil. HCl (1 :1) and 100 cc. of water. Heat in a boiling water bath for 2.5 hours. Cool and nearly neutralize to litmus paper with NaOH. Dilute to 500 cc. in a volumetric flask, pipette out 50 cc. (equivalent to 0.4 gram of the original) and determine the reducing sugars by the Munson and Walker method as described above under Dextrose. Calculate the total reducing sugars as dextrose. Subtract from this figure the percentage of dextrose, previously determined, and multiply the difference by 0.9 to obtain the percentage of dextrin.

NOTE.—By this method the amount of soluble starch, if any, is included with the dextrin, but as their properties are, for most purposes, quite similar, the additional work involved in the separation is not usually worth while.

Viscosity.—Determine the viscosity by means of a Dudley pipette at 25° C. Standardize the pipette with a sugar solution made by dissolving 120 grams of pure cane sugar in 100 cc. of distilled water at 25° C. This solution should give a viscosity of about 100 seconds. In determining the viscosity, have the pipette surrounded by a jacket containing water at the same temperature. Fill the pipette slightly above the mark with the solution, then set it exactly on the upper mark. Release the solution with one hand and start a stop watch with the other. Determine the number of seconds required by the solution to run from the top mark to the bottom mark. Make several determinations and report the average. After standardizing the pipette with sugar solution determine the viscosity of a solution of the sample in the same way. Mix 40 grams of the sample with about 150 cc. of distilled water, heat to boiling for exactly 1 minute, stirring thoroughly; transfer to a 200-cc. volumetric flask, cool and make up to volume at 25° C. Use this solution for the viscosity determination.

NOTE.—The viscosity of the solution depends largely on the time of heating. The material should be stirred up with a little warm water and then transferred rapidly to a beaker containing the rest of the water, which

should be near the boiling point. It should be rapidly heated to boiling and boiled for exactly 1 minute.

ALBUMIN

General.—Commercial albumin is chiefly from two sources, eggs and blood-serum. The latter is cheaper than egg albumin and has a better thickening power. It is largely used for fixing dyes and pigments in calico printing in all but the finest colors. The blood-serum albumin varies from a dirty yellow color to the black color of "dried blood." Egg albumin is generally transparent and of a light yellow color. It should be free from blisters which indicate partial coagulation. On treatment with cold water, commercial albumin of good quality should dissolve almost completely. In making the test, the albumin should always be added to the water and not *vice versa*. (If it is desired to keep the solution, add about 1% of arsenious oxide.)

Qualitative Tests.—Commercial albumin is frequently adulterated with dextrin, gums, sugar, flour, etc. For qualitative examination grind to a powder and add 5 grams (accurately weighed) slowly to about 50 cc. of water until the soluble matter is dissolved. Pure and high-grade samples should leave no residue. Add a few drops of acetic acid and filter through silk or fine muslin into a 500-cc. volumetric flask. The insoluble residue may consist of coagulated albumin, casein, starch, or membranous matter. Treat it with very dilute NaOH solution, filter and then exactly neutralize the filtrate with acetic acid. If casein is present, it will be dissolved by the NaOH and precipitated on neutralization.

Make the original filtrate up to 500 cc. Pour about 100 cc. into a beaker and heat to boiling. This should coagulate the albumin. Filter and treat the filtrate with a little acetic acid and potassium ferrocyanide to make sure that no proteins remain in the solution. If there is a precipitate, filter it out. (A precipitate generally indicates casein, although it must be remembered that any Zn would be thrown out as white ferrocyanide.) Cool the filtrate and add a little conc. tannic acid solution. This will precipitate any gelatin or glue. Filter, and concentrate the filtrate to a small bulk. Cool and treat with a considerable excess of alcohol. Any precipitate indicates the presence of gums or dextrin. Filter, boil off all the alcohol, heat with dil

HCl and test the solution in the usual way with Fehling's solution after neutralizing the excess of HCl. Any reduction indicates the presence of sugar but does not necessarily prove its presence. Sugar may also be extracted by treating the original solid sample with alcohol.

Soluble Coagulable Albumin.—Pipette 100 cc. of the original water solution (equivalent to 1 gram) into a beaker. Add about 1 gram of sodium acetate and heat to boiling. Filter the flocculent precipitate on a tared filter using a platinum cone and suction. Wash with hot water, dry at 100° C. and weigh.

Moisture.—Dry 2 grams of the material in a weighed porcelain dish to constant weight at 100° C. Report the loss as Moisture.

Ash.—Instead of determining the actual residue on ignition in the usual way, it is better on account of the fusible nature of the ash to proceed as follows:

Treat the residue from the moisture determination with a few drops of conc. HNO_3 and 2 or 3 drops of H_2SO_4. On heating gently, the albumin dissolves to a clear yellow liquid which may be evaporated to dryness without trouble. Ignite the dry residue to constant weight and report the result as "sulfated ash." Allen gives the following results obtained on various samples:

TABLE V—SULFATED ASH OF ALBUMINS

	Designation.	Sulfated ash, per cent
Egg albumin	No. 1	7.4
Egg albumin	No. 2	7.0
Blood-serum albumin	Refined	9.1
Blood-serum albumin	Prime	8.5
Blood-serum albumin	No. 1	9.2
Blood-serum albumin	No. 2	8.9
Blood-serum albumin	No. 3	9.7
Blood-serum albumin	Black	6.2

The addition of sugar or dextrin to the albumin would lower the amount of ash. If it is abnormally high, it may also be examined for Zn or other inorganic materials.

REFERENCE.—Allen: "Commercial Organic Analysis." 2d ed., 4, 44 (1898).

TANNIC ACID

General.—Many processes have been devised for estimating tannic acid in the substances known as "tannins." Most of these methods, however, have had in view the valuation of tannins for tanning leather, but it does not necessarily follow that they are equally serviceable for valuing tannins when used in dyeing.

Proctor's modification of Loewenthal's method has been very generally adopted both for tanning and dyeing purposes. Nevertheless, if the tannin is to be used in the leather industries, the Loewenthal method of analysis should not be used. In such cases use the Official Method of the American Leather Chemists' Association.

The determinations most generally required on tannins or tannic acid for dyeing purposes are as follows:

Moisture.—Weigh 1 gram if the material is solid, 5 grams if liquid, in a platinum crucible or dish and dry at 100° C. to constant weight. Report the loss in weight as moisture.

Ash.—Ignite the above, carefully at first, and finally to the full heat of the Bunsen burner; cool in a desiccator and weigh.

Total Astringency (Loewenthal-Proctor Method).—Dissolve 1 gram of the solid in water and dilute to 1 liter. If the sample is a liquid, dilute 5 grams to 1 liter. Pipette 10 cc. of this solution into a large porcelain dish containing 750 cc. of water. Add 25 cc. of indigo carmine solution and titrate with standard $KMnO_4$ exactly as under Sumac analysis (p. 750).

Astringent Non-tannins.—To 50 cc. of the above solution in a strong 8-ounce bottle, add 25 cc. of 2% gelatin solution, 25 cc. of saturated NaCl acid solution and 10 grams of china clay. Shake thoroughly for about 5 minutes and filter through a dry filter. This removes the tannins. Test a portion of the filtrate with more of the gelatin solution to see if precipitation is complete. (If not complete, make up a gelatin solution stronger than 2% and repeat the process, using 25 cc. of the latter solution.) Titrate 20 cc. of this filtrate, equivalent to 10 cc. of the original solution, and calculate the percentage of astringent non-tannins.

Tannic Acids or Tannins.—The difference between the total astringency, calculated as tannin, and the astringent non-tannins gives the percentage of tannins.

NOTES.—(1) The solutions referred to above are made as follows:

(*a*) *Indigo Carmine Solution.*—Dissolve 5 grams of pure indigo carmine in water, add 50 grams of conc. H_2SO_4 and dilute to 1 liter. If indigo carmine is not available, sulfonate 1 gram of pure indigo with 60 cc. of conc. H_2SO_4 for 6 hours at 70–80° C. and dilute with water to 1 liter.

(*b*) *$KMnO_4$ Solution (approx. 0.01 N).*—This should be accurately standardized against oxalic acid or sodium oxalate.

(*c*) *Gelatin Solution.*—Soak 20 grams of Nelson's gelatin in water for 2 or 3 hours. Then dissolve on the steam bath with the addition of more water and dilute to 1 liter.

(*d*) *Saturated NaCl Acid Solution.*—Make up a 5% solution of H_2SO_4 and saturate with ordinary salt.

(2) In calculating the tannin titrations use the factor 1 cc. 0.01 N $KMnO_4$ = 0.0004157 gram tannin.

(3) It is often customary in analyzing mixed tannins or extracts containing tannin to calculate the tannin in terms of oxalic acid.

1 cc. 0.01 N $KMnO_4$ = 0.0006302 gram $H_2C_2O_4 \cdot 2H_2O$.

(4) The above method is especially intended for pure tannic acid and tannins for use in dyeing.

REFERENCE.—Knecht-Rawson-Loewenthal: "Manual of Dyeing," 8th ed., **2,** 802.

INDIGO

POWDER OR PASTE

General.—The methods employed for testing indigo may be broadly classified into three groups:

(1) Conversion into sulfonic acid.

(*a*) Indigotin estimated by oxidation.

(*b*) Indigotin estimated by reduction.

(2) Indigotin reduced in an alkaline solution, the indigotin re-oxidized, separated, purified, and weighed, or dissolved in acid and titrated as in (1).

(3) Extraction by volatile solvents.

There are two kinds of indigo encountered commercially, natural and synthetic. At the present time the synthetic has practically replaced the natural. The natural indigo usually comes in the form of lumps and contains besides indigo blue, or indigotin, other substances both of organic and inorganic nature which owe their presence to the process of manufacture. Their amount varies according to the quantity of indigo blue that is contained in the sample and varies widely in indigoes of different origin. The mineral impurities consist of sand, silicates, and

$CaCO_3$. The organic impurities consist of (1) indigo gluten or gum, (2) indigo brown, and (3) indigo red or indirubin.

Synthetic indigo is practically pure indigotin and is usually put out in the form of a paste containing about 20% indigotin and 80% water.

Moisture.—If the sample is in the form of lumps, grind to a fine powder and dry 1 gram at 100–105° C. to constant weight. If the sample is in the form of a paste, mix thoroughly, weigh out as rapidly as possible 10–15 grams and dry to constant weight at 100–105° C. Report loss in weight as Moisture.

Indigotin. (By reduction with hydrosulfite.)—This method gives the most exact figures for the indigotin content and is not influenced by the impurities contained in the indigo. It also is the quickest method and the danger of errors is reduced to a minimum owing to the change in color being very easy to recognize.

Sulfonation.—Weigh accurately 1 gram of the very finely powdered dry indigo and heat for 5 hours with 6 cc. of conc. H_2SO_4 at 105–120° F. with frequent stirring, then pour into water and make up to 1 liter. In the case of natural indigo there is usually an insoluble residue which, however, contains no indigotin. The temperature should not be allowed to exceed 120° F. as otherwise much darker solutions are obtained, which render the titration more difficult.

Preparation of Solutions.—Any freshly prepared solution of sodium hydrosulfite may be used as a titrating solution, provided that it does not contain more than 1% alkali. It is advisable to use a hydrosulfite solution of such strength that 25–30 cc. will decolorize 0.1 gram of indigo or 100 cc. of a 0.1% solution of indigo. To prepare the hydrosulfite solution mix 400 cc. of sodium bisulfite liquor of sp. gr. 1.36–1.38 (72–76° Tw.) with 950 cc. of water, and then add 35 grams of zinc powder which has been previously worked to a paste with 50 cc. of water. The zinc paste should all be added within 15 minutes in small portions, stirring or shaking gently. After the mixture has stood for 1 hour, draw off the clear liquid into lime water prepared by slaking 45 grams of good quicklime with 200 cc. of hot water. Stir the mixture for some time and then let it stand quietly for about 12 hours. Then draw off the clear hydrosulfite solution and add for every

liter 5 cc. of NaOH solution of sp. gr. 1.38 (76° Tw.). The solution should show a distinctly alkaline reaction. If it does not, add a little more NaOH solution.

Standardization of Hydrosulfite Solution.—Weigh out accurately 1 gram of pure standard indigo powder of known indigotin content and sulfonate as above described under Sulfonation. Make this up to 1 liter with water. Pipette 100 cc. of this solution into a flask and run in from a burette the hydrosulfite solution until all the blue color has disappeared. A stream of CO_2 or illuminating gas must be run into the titrating flask to expel all air and have a reducing atmosphere before the titration is begun. The tip of the burette should be drawn out to a point about 8–10 cm. long. Have this tip below the surface of the liquid until the blue color has nearly disappeared. Then raise the tip and run in, drop by drop, the hydrosulfite solution until all the color has disappeared. This must be done as rapidly as possible to prevent oxidation.

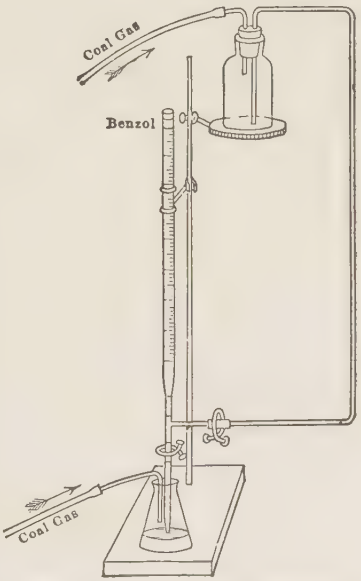

FIG. 5.—Apparatus for Titrating Indigotin.

From the titration calculate the strength of the hydrosulfite solution in terms of indigotin. Then dilute so that it requires 25–30 cc. to decolorize 100 cc. of the standard indigotin solution. Retitrate this corrected solution and determine the exact strength in terms of indigotin. Before making the final titration, place the hydrosulfite solution in a 2-liter bottle and pour in sufficient benzol to form a layer 1–2 cm. deep to exclude the air. Also connect up the bottle so that a stream of illuminating gas can be passed into it (see Fig. 5).

TITRATION OF SULFONATED SAMPLE.—Pipette into the titrating flask an aliquot of the solution prepared as described under Sulfonation which will correspond to about 0.1 gram of indigotin,

and titrate with the hydrosulfite solution exactly as in the standardization. This should require at least 25 cc. of hydrosulfite solution. If less is required, repeat, using a larger aliquot. Always run the titration in duplicate.

NOTE.—The titration must be made as rapidly as possible and at the same time *great care* must be used not to overrun the end-point. If the titration is carried out too slowly, there is danger of the indigo solution oxidizing back to indigo blue and the results will be too high. With a little experience there should not be much difficulty in determining the end-point, especially with synthetic indigoes, but with the impure natural indigoes there is apt to be some trouble in determining the exact end-point and it is best, especially if one is not familiar with the titration, to run several titrations and report the average.

Mineral Matter (Ash).—Weigh accurately 1 gram of the dried powder into a platinum dish and ignite *gently* until all organic matter is burned off. As $CaCO_3$ is generally present, care should be taken not to ignite sufficiently to drive off the CO_2. For more accurate work blast the ash, determine quantitatively the CaO, calculate it to $CaCO_3$ and correct the mineral matter accordingly.

REFERENCE.—Badische Anilin- u. Soda-Fabrik: "Indigo Pure," 26.

TOBACCO AND TOBACCO EXTRACT

General.—The samples should be analyzed as received, as any attempt at artificial drying is likely to cause loss of nicotine. (If the tobacco is too moist to be ground, it may be dried at a temperature not exceeding 60° C.) The material should be ground so as to pass through a No. 20 sieve or finer.

Nicotine (Silicotungstic Acid Method).—Distill the sample in a current of steam as described below and precipitate the nicotine from the distillate as nicotine-silicotungstate, a rose-white salt with the following formula:

$$2C_{10}H_{14}N_2 \cdot 2H_2OSiO_2 \cdot 12WO_3 \cdot 5H_2O.$$

This salt on being ignited leaves a residue of SiO_2 and WO_3, from which is calculated the weight of nicotine originally present.

REAGENTS.—(*a*) *Silicotungstic Acid Solution.*—Prepare a 12% solution of the silicotungstic acid having the following formula: $4H_2OSiO_2 \cdot 12WO_3 \cdot 22H_2O$.*

(*b*) *Sodium Hydroxide Solution.*—Dissolve 400 grams of NaOH in water and dilute to 1 liter.

(*c*) *Dilute Hydrochloric Acid* (1 : 4).

DETERMINATION.—Weigh such an amount of the sample as will contain preferably between 0.1 and 1.0 gram of nicotine (if the sample contains very little nicotine, about 0.1%, do not increase the amount to the point where it interferes with the distillation); wash with water into a 500-cc. round-bottomed distillation flask; add a little paraffin to prevent frothing, a few small pieces of pumice and a slight excess of the NaOH solution, using phenolphthalein as an indicator. Distill rapidly in a current of steam through a well-cooled condenser, connected by an adaptor with a suitable flask containing 10 cc. of the dil. HCl. When distillation is well under way, heat the distillation flask to reduce the volume of the liquid as far as practicable without bumping or undue separation of insoluble matter. Distill until a few cc. of the distillate show no cloud or opalescence when treated with a drop of silicotungstic acid and a drop of the dil. HCl. Confirm the alkalinity of the residue in the distillation flask with phenolphthalein. Make up the distillate, which may amount to 1000–1500 cc. to a convenient volume (the solution may be concentrated on the steam bath without loss of nicotine); mix well and pass through a large dry filter if not clear. Test a portion with methyl orange to confirm its acidity. Pipette an aliquot, containing about 0.1 gram of nicotine, into a beaker (if the samples contain very small amounts of nicotine, an aliquot containing as little as 0.01 gram nicotine may be used); add to each 100 cc. of liquid 3 cc. of the dil. HCl, or more if the necessity is indicated by the test with methyl orange, and add 1 cc. of silicontungstic acid solution for each 0.01 gram of nicotine supposed to be present. Stir thoroughly and let stand overnight. Before filtering, stir the precipitate to see that it settles quickly and is in crystalline form; then filter on an ashless filter paper, and wash

* There are several silicotungstic acids. Those having the formulas $4H_2OSiO_2 \cdot 10WO_3 \cdot 3H_2O$ and $4H_2OSiO_2 \cdot 12WO_3 \cdot 20H_2O$ do not give crystalline precipitates with nicotine and should not be used.

with cold dil. HCl (1 : 1000). Transfer the paper and precipitate to a weighed platinum crucible, dry carefully, and ignite until all carbon is destroyed. Finally heat over a Teclu or Meker burner for not more than 10 minutes. The weight of the residue multiplied by 0.114* gives the weight of nicotine present in the aliquot. Calculate as percentage of the original sample.

Ash.—Incinerate 2 grams of the sample in a weighed platinum dish. Moisten with water, dry and again ignite. Repeat until no more particles of carbon remain. Cool in a desiccator and weigh.

Dissolve the ash in hot water and filter. Save the filtrate. Ignite and weigh the water-insoluble ash. Cool the filtrate and titrate with 0.1 N acid and methyl orange. Report the alkalinity of the water-soluble ash as the number of cc. of 0.1 N acid required to neutralize the water-soluble ash from 1 gram of the sample.

Dissolve the water-insoluble ash in 25 cc. of 0.5 N HCl and titrate the excess with 0.1 N alkali and methyl orange. Deduct the number of cc. of 0.1 N alkali from 125 and divide by 2. This will give the alkalinity of the water-insoluble ash in the same terms as above. (In some cases it may be necessary to use double the amount of 0.5 N acid. In that case subtract the cc. of 0.1 N alkali from 250 and divide by 2.)

After titration of the water-insoluble ash, add conc. HCl and boil. Filter the bulk of the solution through an ashless filter and add conc. HCl to the residue. Warm, dilute and filter through the same filter. Wash with distilled water, ignite, weigh and report as percentage of Hydrochloric Acid-insoluble Ash.

NOTES.—(1) Cigarette tobacco contains about 1.0–3.3% of nicotine (average about 1.7%), cigars about 1.5%, chewing tobacco about 1.1%.

(2) *Cigarette papers.* Nearly all cigarette papers have chemical fillers, presumably to improve their burning qualities and color. These generally consist of carbonates and oxides of Al, Ca and Mg. The best papers are made from pure linen sized with starch. A little KNO_3 is also sometimes added.

REFERENCES.—Azor Thurston: "Analysis of Cigarettes, Cigars and Tobacco," *Bull.* 2, Agricultural Commission of Ohio, Dairy and Food Div., Bureau of Drugs, November, 1914. Association of Official Agricultural Chemists.: "Methods of Analysis," p. 66 (1925).

* The factor 0.1140 is given in the official A.O.A.C. method. The theoretical factor is 0.1117.

NICOTINE SOLUTION

General.—This method is for the analysis of nicotine solutions for use in preparing specially denatured alcohol according to Formula No. 4. The tobacco denaturant must conform to the following analytical requirements:

Determination of Nicotine.—Measure 20 cc. of the solution into a special 250-cc. dephlegmating flask (Fig. 6);* add 50 cc. of 0.1 N NaOH and distill in a current of steam until the distillate is no longer alkaline (about 500 cc.). Wash the distillate into a

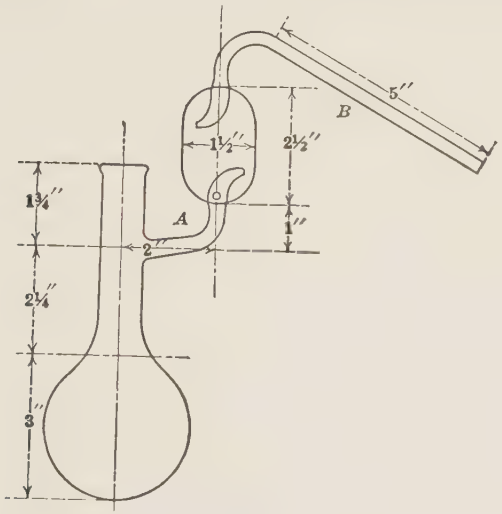

FIG. 6.—Flask for Nicotine Determination.

700-cc. flask and fill two other flasks with the same amount of distilled water. Add 8 drops of resazurin solution† to each flask as an indicator, and add 1 drop of 0.1 N acid to one blank and 1 drop of 0.1 N alkali to the other. This should give in the case of the acid solution a pink coloration and in the case of the alkali solution a blue coloration by transmitted light. Then titrate

* *Regulations* No. 30, U. S. Internal Revenue specifies a Kjeldahl flask fitted with a suitable bulb tube, but we have found the special flask more convenient and equally accurate.

† *Resazurin Solution:* Dissolve 0.2 gram of the crystals in distilled water add 40 cc. of 0.1 N NH_3 solution and dilute to 1 liter.

the nicotine distillate with 0.1 N H_2SO_4 and make comparisons with the 2 blanks until the nicotine distillate shows an end-point of all red and no blue on transmitted light. This end-point is difficult to detect without some practice and it should be approached with care. The best way to observe the final end-point is to place all three flasks in a line on white paper and have a sheet of white paper back of them. A comparison of color can be made much more easily in this way. Not less than 23.2 cc. of 0.1 N H_2SO_4 should be required for the neutralization. (This is equivalent to 1.88% of nicotine, which is the minimum amount required in the tobacco denaturant.)

CALCULATION.—

$$\text{Cc. 0.1 N } H_2SO_4 \text{ required} \times \frac{0.16213}{2} = \text{percentage of nicotine.}$$

Test of Coloring Matter.—The original formula for nicotine denaturant required that it be colored with a mixture of blue and yellow dyes, thus giving a green solution. On Aug. 11, 1916, due to the scarcity of dyestuffs, the Treasury Department ruled that the yellow dye may be omitted and the denaturant colored only with methylene blue.

In case the denaturant is of a *green* color, proceed as follows for the test of coloring matter:

Take 1 cc. of the denaturant and make up to 100 cc. with water, acidulating with a few drops of H_2SO_4. Immerse in this solution a piece of white cotton cloth and boil the solution. Continue the process, adding more cloth and more water if necessary, until all the blue color in the solution is fixed on the cloth. Then add a piece of white woolen cloth and boil the bath as before until all the yellow color is fixed upon the cloth. Both the cotton and woolen cloths should show decided colors—the cotton blue and the woolen yellow.

If the denaturant is *blue*, no dyeing test is required.

Intensity of Color.—If the denaturant is *green*, it must contain sufficient coloring matter so that when observed in an eighth-inch cell of Lovibond's tintometer it will show a color of an intensity not less than No. 24 yellow combined with No. 3 blue.

If the denaturant is *blue*, proceed as follows: Dilute 1 cc. of the denaturant material with 100 cc. of water and compare 50 cc. of this solution in a 50-cc. Nessler tube with 50 cc. of a solution

containing 5 grams of copper sulfate ($CuSO_4 \cdot 5H_2O$) in 100 cc. of water. The color of the diluted nicotine solution should be at least as intense as that of the copper solution.

NOTES.—(1) The original regulations called for the use of rosolic acid as indicator. Resazurin, however, gives a better end-point and in a letter from the Commissioner of Internal Revenue at Washington, dated Sept. 4, 1913, the use of the latter was sanctioned.

(2) Resazurin crystals are made by Dr. Theodore Schuchardt, Corlitz, Germany, and may be obtained from Eimer & Amend, New York, N. Y. and from Coleman and Bell Co., Norwood, Ohio.

(3) If the nicotine solution has stood for some time in the sunlight before analysis, the blue color may have partially faded out. Before rejecting a sample on account of deficiency of blue color, therefore, blow a stream of air through it for a few minutes to reoxidize any reduced dye and repeat the test for intensity of color on the aerated portion.

REFERENCES.—*Regulations* No. 30, Revised, U. S. Internal Revenue (July 15, 1907); appendix to *Regulations* No. 61, Revised, U. S. Internal Revenue (August, 1925); Treasury Decision 1223 (Sept. 5, 1907).

DIASTATIC POWER OF MALT

(Lintner Value)

General.—The determination of diastatic activity or Lintner Value, *i.e.*, power of converting starch into dextrose, is the most important test in the examination of malt and malt flours, and is generally used as the basis of purchase. When 0.1 cc. of a 1:20 extract of malt will invert sufficient starch to reduce 5 cc. of mixed Fehling's Solution, its Lintner Value is 100.

There are numerous methods in use, none of which is entirely satisfactory. To get satisfactory results it is very important that the water used for reagents and for preparing the extract should be free from NH_4 compounds, nitrites and other impurities which may influence the diastatic conversion. Water should be redistilled with the addition of a little $KMnO_4$ and NaOH, and the distillate should be neutral to litmus or alizarin paste. When two chemists are attempting to make check determinations on the same sample, it is necessary not only that exactly the same procedure be employed but that they use the same starch. Of the following procedures Method 1 is that devised by A. R. Ling, and is perhaps most widely used. Method 2 is the Seyffert Modification. It is much shorter, gives approximately the same results, and is largely employed as a control test.

Before determining the diastatic power of any malt which is in dispute, agreement should be reached between the parties interested regarding the method to be employed.

Preparation of Sample.—If the sample is an extract, no further preparation is required except proper dilution. If the sample is the original malt, grind it finely, weigh out 25 grams and digest with 500 cc. of distilled water for 3 hours at 70° F., stirring the mixture well every half hour. Filter through a dry filter, rejecting the first 100 cc. of filtrate.

Solutions.—The following solutions are required:

Starch Solution.—Dissolve in boiling water in the proportions of 2 grams of soluble starch per 100 cc. of water. Then cool the solution to 70° F. for use. It should be mobile (not gelatinous), indicating perfect conversion into soluble starch, and show only negligible reducing action on Fehling's solution; and it should be neutral to litmus solution.

Soluble starch for Lintner determinations may be purchased from dealers in C. P. chemicals. The method of preparation is as follows: Digest 500 grams of purified potato starch with 1 liter of dil. HCl (1:4) at room temperature (60–65° F.) for 7 days, stirring the mixture daily. Wash the mass very thoroughly by decantation, at first with tap water and later with distilled water, until the wash water is free from acid. Collect on a filter paper placed in a Büchner funnel, suck as dry as possible, and then spread out on a new unglazed plate. Dry the starch at gentle heat (110° F.) as quickly as possible. When dry, triturate in a porcelain mortar and rub through a fine hair sieve.

Fehling's Solution.—(1) Dissolve 30.64 grams of pure crystallized copper sulfate, free from iron and moisture, in water and dilute to 500 cc.

(2) Dissolve 70 grams of NaOH of good quality (not less than 97% NaOH) and 175 grams of recrystallized potassium sodium tartrate in about 400 cc. of water and dilute the solution to 500 cc.

For use add the $CuSO_4$ solution carefully to an equal volume of the alkaline tartrate solution. (They keep much better if the two solutions are preserved in separate bottles and mixed as needed.) Use 5 cc. of the mixture for each determination.

Determination.—*Method* 1.—Let 3 cc. of the perfectly clear and bright extract act on 100 cc. of a 2% solution of soluble

starch at 70° F. for 1 hour in a 200-cc. volumetric flask; then add 10 cc. of 0.1 N NaOH solution to stop further diastatic action. Cool to 60° F. and make up to 200 cc. with water at the same temperature. Shake well and titrate as follows against 5-cc. portions of Fehling's solution, using as an outside indicator a double filter moistened with a fresh solution of $K_4Fe(CN)_6$ acidified with acetic acid:

Pipette 5 cc. of mixed Fehling's solution into a 150-cc. flask and heat to boiling over a small flame; then add the converted starch solution from a burette, in small quantities at first of about 5 cc., keeping the mixture rotated and boiling after each addition, until the reduction of copper is complete, as determined by rapidly withdrawing a drop of the liquid on a glass rod and bringing it at once into contact with the indicator.

Calculate the Lintner Value from the formula $L = \frac{1000}{XY}$; where L = diastatic power (Lintner Value); X = cc. of malt extract contained in 100 cc. of the fully diluted starch conversion liquid, *i.e.*, one-half the amount originally added to the 100 cc. of starch liquid; and Y = cc. of the same liquid required for reduction of 5 cc. of mixed Fehling's solution.

NOTE.—The above method (using 3 cc. of malt extract to 100 cc. of 2% soluble starch solution) is not accurate for malts having a diastatic capacity exceeding 50 Lintner. In the case of such malts the relative volume of malt extract taken must be less, say 2 cc., or for malts of the highest diastatic capacity, such as are frequently used by distillers and vinegar makers (over 80 Lintner) an even smaller amount of extract must be taken. The production of maltose should not exceed 45% of the starch used (5 cc. of mixed Fehling's solution = 0.04 gram of maltose).

Method 2.—With a 1-cc. Mohr pipette graduated to hundredths measure accurately into a series of sixteen carefully cleaned test-tubes the following amounts of the malt extract prepared as previously described, namely, 0.10, 0.11, 0.12, 0.14, 0.16, 0.18, 0.20, 0.22, 0.25, 0.28, 0.33, 0.40, 0.50, 0.70, 1.0 and 2.0 cc. Note the time, and in each tube quickly place 10 cc. of 2% starch solution. Mix the contents of the tubes by gently shaking, without letting the liquid touch the hand. Then place in a water bath at 70° F. Shake again after 20 minutes, 40 minutes, and 1 hour, respectively. At the end of 1 hour place 5 cc. of mixed Fehling's

solution in each tube in the same rotation as before and mix thoroughly by shaking. This may now be done by placing the thumb over the mouth of the tube. Replace the tube in the holder, and keep in the boiling water for 10 minutes. Some of the tubes will be yellow, where there is excess of malt solution; others blue, due to excess of Fehling's solution. Select the tube which is neither blue nor yellow, or 2 adjacent tubes of which one is yellow and the other blue. In the first case the Lintner value may be read directly from Table VI, knowing the cc. of malt extract added to the tube. In the other case calculate the Lintner values corresponding to the two adjacent tubes and take the average.

If the intervals between the two test-tubes are too great, the determination should be repeated, bringing them nearer together. If the Lintner value is over 80, the original malt solution should be diluted with an equal volume of water before carrying out the tests, and Lintner values obtained must be multiplied by 2. In the case of extremely high Lintner values the malt solution should be still further diluted and corresponding multiplication made of the observed value. For this reason it is advisable to make a preliminary test, say with 0.1 cc. and 0.2 cc. of malt extract, to decide what dilution and how many tubes are necessary.

In case the blue color of the unreduced Fehling's solution is too faint to allow the critical point to be selected by the eye, test for Cu in the following manner: Filter about 2 cc. of the contents of the tube to be tested through a double filter, add about an equal volume of acetic acid, mix thoroughly and pour half into another test tube. To one of the tubes add 1 drop of a weak solution of $K_4Fe(CN)_6$ and observe any change in color. The presence of Cu will be indicated by a dirty red. The $K_4Fe(CN)_6$ solution should be prepared fresh by dissolving a small piece about the size of a pea in about 10 cc. of water.

TABLE VI—CALCULATION OF LINTNER VALUE
(Seyffert Modification)

Malt extract, cc.	Lintner value	Malt extract, cc.	Lintner value	Malt extract, cc.	Lintner value
0.100	100.00	0.220	45.5	0.38	26.3
0.105	95.2	0.225	44.5	0.39	25.6
0.110	90.9	0.230	43.5	0.40	25.0
0.115	87.0	0.235	42.6	0.45	22.2
0.120	83.3	0.240	41.7	0.50	20.0
0.125	80.0	0.245	40.8	0.55	18.2
0.130	76.9	0.250	40.0	0.60	16.7
0.135	74.1	0.255	39.2	0.65	15.4
0.140	71.4	0.260	38.5	0.70	14.3
0.145	69.0	0.265	37.7	0.75	13.3
0.150	66.7	0.270	37.0	0.80	12.5
0.155	64.5	0.275	36.4	0.85	11.8
0.160	62.5	0.280	35.7	0.90	11.1
0.165	60.6	0.285	35.1	0.95	10.5
0.170	58.8	0.290	34.5	1.00	10.0
0.175	57.1	0.295	33.9	1.10	9.1
0.180	55.6	0.30	33.3	1.25	8.0
0.185	54.1	0.31	32.3	1.40	7.1
0.190	52.6	0.32	31.3	1.60	6.3
0.195	51.3	0.33	30.3	2.00	5.0
0.200	50.0	0.34	29.4	2.50	4.0
0.205	48.8	0.35	28.6	3.30	3.0
0.210	47.6	0.36	27.8	5.00	2.0
0.215	46.5	0.37	27.0	10.00	1.0

REFERENCE.—Allen: "Commercial Organic Analysis," 4th ed., **1**, 136 (1915).

CHAPTER IV

ANALYSIS OF METALS

SAMPLING IRON AND STEEL

General.—Select at random a sufficient number of bars, rods, rails, I-beams, or car axles, etc., as the case may be, to represent the shipment and carefully mark them. From each of these pieces procure a sample composed of mixed borings weighing between 1 and 2 ounces.

Location of Borings.—In order to eliminate as far as possible the effect of possible segregation, take the borings at different points of the piece, selection being made with reference to the rapidity with which the different portions may have cooled. This is preferably done on a cross-section of the piece. For example, in sampling a steel rail, make one boring close to the outside of the head, one at the center of the head, another at the middle of the web, and one near the center of the foot. Where access to a cross-section is impossible, take borings from the outside which will represent as nearly as possible the desired location.

Cleaning the Surface.—When borings are to be made from a longitudinal surface, remove all rust and scale by means of an emery wheel, emery cloth, or other abrasive; in no case, however, should any considerable portion of the first borings be discarded. When drilling into a cross-section, discard enough of the borings to insure absence of rust or dirt from the portion taken.

Size of Borings.—In order that a perfect mixing of the samples from different parts of the piece may be possible, it is desirable to have borings in the form of small thin chips, rather than long, spiral turnings. This may be accomplished by slightly dulling the cutting edge of a half-inch twist drill or by using a half-inch flat drill.

Freedom from Contamination.—It is absolutely essential that the utmost care be taken to prevent contamination of the sample with grease, oil, or dirt of any kind. Brush the piece of iron or

steel to be sampled free from any loose material which may adhere to it; collect the borings on a clean white sheet of paper. Use no oil, grease, or other lubricating substance on the drill.

Place the combined borings from each piece in clean, wide-mouthed, glass-stoppered bottles; stopper tightly and carefully mark each bottle for identification.

CARBON STEEL

General.—This method covers the analysis of plain carbon steels, *i.e.*, those containing only C, Mn, P, Si and S.

In those cases where an alternative method is given, the latter is to be used only when for some special reason the first method cannot be employed.

Preparation of Sample.—The points to be observed in sampling steel for analysis are as follows:

(1) Samples must be drillings or chips cut by some machine tool without the application of water, oil, or other lubricant, and free from scale, grease, dirt or other foreign substance. If samples are taken by drilling, the diameter of the drill should be not less than 0.5 nor more than 0.75 inch.

(2) Samples must be uniformly fine and well mixed before analysis.

(3) If the composition of the surface of a sample piece has been altered by case hardening or decarbonization, do not include in the sample for analysis drillings which represent this outer surface.

(4) Heat-treated samples should be annealed before sampling.

(5) Round or flat samples up to and including 1 inch in thickness must be drilled through the entire thickness of metal; or, if the sample is taken on a milling machine, it must be taken by machining off the entire cross-section.

(6) From material having a cross-section larger than 1 inch samples should be taken at any point midway between the outside and the center by drilling parallel to the axis. If this is not practicable, the piece may be drilled on its side, but do not collect the drillings until they represent the above-named portion of the sample.

(7) Whenever a sample is received in the form of drillings, they should always be examined for oil and other foreign matter.

Any oil must be completely removed with ether and the drillings then thoroughly dried. If foreign particles are present, go over the sample with a magnet and use only that portion for analysis which is picked up by it.

Total Carbon.—Determine the total carbon by direct combustion in the electric furnace. The general arrangement of the combustion apparatus is as follows (see Fig. 7):

(*a*) Oxygen tank.

(*b*) Safety jar for H_2SO_4.

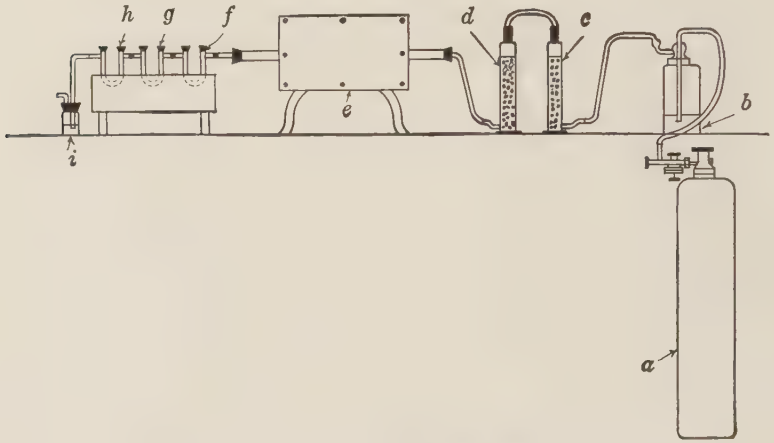

Fig. 7.—Apparatus for Determining Carbon in Steel.

(*c*) $CaCl_2$ jar.

(*d*) Soda-lime jar.

(*e*) Hoskins' multiple-tube electric furnace.

(*f*) U-tube for granular Zn.

(*g*) U-tube for $CaCl_2$.

(*h*) Soda-lime absorption tube for CO_2.

(*i*) Bottle for $Ba(OH)_2$ solution (exhaustion and gas speed indicator).

The combustion apparatus should be tested for leaks from time to time (see Blair: "Chemical Analysis of Iron," p. 138, Fig. 63). Before weighing the absorption tubes in the morning connect them to the combustion apparatus and pass oxygen through for 10 minutes; weigh and again pass oxygen through for

30 minutes and weigh. This should be continued until the weight is constant.

For steels containing 0.30–1.50% carbon, take 2 grams of fine drillings not over 0.25 mm. thick. For lower percentages of C, take 3–5 grams of drillings between 20- and 60-mesh size. Transfer the sample to an alundum or clay boat, protected by a layer of ignited Al_2O_3 or alundum. Place the drillings in as compact a mass as possible. If curly drillings are scattered along the entire length of the boat instead of being put in a deep, compact body, borings that are a little thick will frequently be found to contain still unburned metal. Drillings lying in close contact heat each other to incandescence during burning with oxygen.

Introduce the boat with the charge into the center of the combustion tube, maintained at a temperature of 1000° C. Admit oxygen at the rate of 25 bubbles per 10 seconds or 250 cc. every 10 minutes. As soon as the steel begins to burn, there is at first a rapid evolution of gas, which quickly ceases. When oxidation of the charge is completed, oxygen begins to flow at normal speed again. Allow 30 minutes for oxidation of the sample and sweeping of all CO_2 from the combustion tube into the absorption apparatus.

Weigh the absorption tube and from the weight of CO_2 calculate the percentage of C in the sample.

CALCULATION.—$CO_2 \times 0.2727 = C$.

NOTES.—(1) In case of very heavy drillings, those that will not pass a 20-mesh sieve, the analysis should be made by solution. Dissolve 2–5 grams of steel, using for each gram 75 cc. of a solution of copper potassium chloride. Follow the procedure described for the determination of Total Carbon in Pig and Cast Iron on page 160. This method, however, is not reliable for alloy steels and should be used on plain steels only when drillings cannot be burned completely by direct combustion.

(2) After refilling the $CaCl_2$ U-tube (*g*) the contents should be saturated with CO_2, as the fresh drier may absorb CO_2 and thereby cause lower results at first.

(3) Soda-lime should be a mixture of the hydroxides of Na and Ca. The most satisfactory soda-lime for carbon combustions in steel is 12-mesh size and contains 15% of water.

(4) Soda-lime absorption tubes should be filled three quarters full with soda-lime and the remainder with $CaCl_2$. The $CaCl_2$ will absorb any moisture which might be liberated by the soda-lime during absorption of CO_2.

(5) Soda-lime tubes will absorb about 0.6-0.7 gram of CO_2 before it is necessary to renew the chemicals. Saturation will be indicated by precipitation of $BaCO_3$ in the $Ba(OH)_2$ solution (*i*).

(6) The same grade of $CaCl_2$ and of soda-lime should be used in the train preceding and following the combustion furnace.

Graphitic Carbon.—Weigh 10 grams of steel in a 200-cc. beaker and add 150 cc. of dil. HNO_3 (1 : 3). Heat the beaker on the steam bath until the steel is all dissolved. Filter on a loose-bottom Gooch crucible through asbestos and wash with water, dil. HCl (1 : 1), water, NH_4OH (1%), water, HCl (1 : 1), water, and again water. Dry for 1 hour at 100° C. Transfer the asbestos with the carbon to the combustion boat and determine the carbon as under Total Carbon.

NOTE.—Carbon is not usually present in steels in the graphitic form. In certain cases, however, particularly in high-carbon steels that have been very slowly cooled, some of the carbon may separate as graphite.

Combined Carbon.—This is the difference between the total and the graphitic carbon.

Manganese (Bismuthate Method).—Titration with sodium arsenite (Method I, below) is sufficiently accurate for ordinary purposes. In case of disputes, however, or where extreme accuracy is desired, the titration should be made with ferrous ammonium sulfate and $KMnO_4$ (Method II). The procedure up to the point of titration is the same in either case, as follows: Dissolve exactly 1 gram of drillings in 50 cc. of dil. HNO_3 (1 : 3) in a 200-cc. Erlenmeyer flask, cool and add about 0.5 gram of sodium bismuthate. Boil until the pink color has disappeared and dissolve any precipitate of MnO_2 by adding a few drops of a saturated solution of $FeSO_4$ or of $Na_2S_2O_3$; then heat until all nitrous oxide fumes have been driven off, cool to 60° F., add 1 gram of Na bismuthate and shake the flask vigorously for a few minutes. Add 50 cc. of 3% HNO_3* and filter the solution into a suction flask through an extra-porous alundum thimble. The thimble should not be filled so full that any of the solution comes in contact with the rubber connection. Wash with 50–100 cc.

* This 3% HNO_3 should be prepared by adding 60 cc. of conc. HNO_3 to 1940 cc. of water; then add 4 or 5 grams of bismuthate, shake and let stand overnight before using. This destroys lower oxides of nitrogen which have a tendency to cause low results.

of the same acid and finally with water. Titrate the filtrate by one of the following methods:

METHOD I.—Titrate the filtrate in the flask with standard sodium arsenite solution until 2 drops produce no further change in color. Until the end-point is reached, the arsenite solution will produce a clear spot where it strikes the liquid.

Sodium Arsenite Solution.—For each liter dissolve 2.5 grams of anhydrous Na_2CO_3 in distilled water, add 1 gram of As_2O_3 to the hot Na_2CO_3 solution and boil until the As_2O_3 is dissolved. Cool and dilute to 1 liter.

Standardization.—Measure into a 300-cc. Erlenmeyer flask exactly 20 cc. of 0.05 N $KMnO_4$ solution. Dilute to 150 cc., add 15 cc. of conc. water-white HNO_3 and titrate with arsenite solution in the same manner as above. Make the standardization in triplicate, and if agreement is satisfactory, take the average. Calculate the Mn factor of the solution.

CALCULATION.—$$\text{Mn factor} = \frac{0.0110}{\text{cc. of arsenite used}}.$$

METHOD II.—Add to the filtrate in the flask an excess of standard ferrous ammonium sulfate solution, then titrate back the excess with 0.05 N $KMnO_4$ solution to the appearance of a faint permanent pink color.

CALCULATION.—Run a blank, exactly as in the regular determination, to obtain the equivalent of the $KMnO_4$ solution in terms of the ferrous ammonium sulfate solution. Subtract the number of cc. of $KMnO_4$ solution used in the back titration from the $KMnO_4$ equivalent of the ferrous ammonium sulfate added. This gives the volume of $KMnO_4$ required by the Mn in the sample, which, multiplied by the Mn factor of the $KMnO_4$, gives the amount of Mn in the sample.

Standard Solutions.—(*a*) 0.05 N $KMnO_4$: Dissolve 1.58 grams of pure $KMnO_4$ in water and dilute to 1 liter.

(*b*) Ferrous Ammonium Sulfate: Dissolve 20 grams of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in water, add 50 cc. of conc. H_2SO_4 and dilute to 1 liter.

Standardization.—Standardize the $KMnO_4$ solution against standard sodium oxalate of the U. S. Bureau of Standards as follows: In a 300-cc. Erlenmeyer flask dissolve 0.150 gram of sodium oxalate in 125 cc. of hot water (80–90° C.) and add 10 cc.

of dil. H_2SO_4 (1 : 1). Titrate at once with the 0.05 N $KMnO_4$, stirring the liquid vigorously and continuously. The $KMnO_4$ must not be added more rapidly than 10–15 cc. per minute, and the last 0.5–1 cc. must be added dropwise, with particular care to allow each drop to be fully decolorized before the next is added. The solution should not be below 60° C. when the end-point is reached.

CALCULATION.—$\text{Mn factor} = \frac{0.0246}{\text{cc. of } KMnO_4 \text{ used}}$.

If the Fe factor of the $KMnO_4$ has already been determined against $Na_2C_2O_4$ as above, the Mn factor may be calculated from the Fe factor by multiplying the latter by 0.1967.

Phosphorus.—Dissolve 2 grams of the sample in a 500-cc. Erlenmeyer flask in 60 cc. of dil. HNO_3 (1 : 3). To the boiling solution, free from red fumes, add 5 cc. of saturated $KMnO_4$ solution. Continue boiling until the pink color disappears. If no precipitate of brown oxide of manganese remains, add a little more $KMnO_4$. When a permanent brown precipitate is produced, cool the flask and add a crystal of tartaric acid. Boil this solution until clear, remove the flask from the hot plate and after 2–3 minutes add 15 cc. of conc. NH_4OH. Bring back with a little HNO_3 if a precipitate of $Fe(OH)_3$ remains. Warm to 80° C., add 60 cc. of molybdate solution and shake for 5 minutes. Let stand 0.5 hour, or until the precipitate settles. Filter at once through an 11-cm. filter paper, wash the yellow precipitate five times with 2% HNO_3, then with 1% KNO_3 solution ($NaNO_3$ must not be used) *until free from acid* (approximately 15 times).

Place the filter and contents in the original flask, which has been thoroughly rinsed with water, add approximately 50 cc. of cold water and a measured excess of standard NaOH solution from a burette, 5 cc. at a time, in sufficient amount to completely dissolve the yellow precipitate. Cork the flask and agitate violently until the filter paper is disintegrated. Add 3 drops of 1% phenolphthalein solution with a medicine dropper and titrate with standard HNO_3 to the disappearance of the pink color.

CALCULATION.—Run a blank titration the same way as in the regular determination to obtain the value of the NaOH solution in terms of the HNO_3 solution. Subtract the number of cc. of HNO_3 used from the number corresponding to the volume of

NaOH added. The difference is the number of cc. of HNO_3 equivalent to the P in the sample. This multiplied by the value of the HNO_3 in terms of P gives the weight of P in the sample. Calculate to percentage.

SOLUTIONS.—*Molybdate Solution:*

(1) 151 grams of MoO_3 (85%).;
600 cc. of water;
150 cc. of conc. NH_4OH.
(2) 1000 cc. of water;
675 cc. of conc. HNO_3;
800 cc. of solution (1).

To prepare solution (1) pour all of the MoO_3 into the water. Shake to get in suspension and, before it settles, quickly pour the NH_4OH into the bottle. Shake until the powder is dissolved. To prepare solution (2) mix the acid and water and *cool thoroughly*. Then by means of a funnel pour in rapidly 800 cc. of solution (1). Shake and add a few crystals of sodium or ammonium phosphate. Shake and let stand overnight before using. Use only the clear supernatant liquid.

Standard Nitric Acid: Dilute 10 cc. of conc. HNO_3 to 1 liter. (The HNO_3 must be water-white.)

Standard Sodium Hydroxide: Dissolve 8 grams of NaOH in 400 cc. of water, add sufficient $Ba(OH)_2$ solution to precipitate all carbonates, filter at once and make up to 1 liter.

1% KNO_3 Solution (for washing): 10 grams per liter.

2% Nitric Acid (for washing): 20 cc. of conc. HNO_3 per liter.

STANDARDIZATION.—First, determine the strength of the standard HNO_3 in terms of the NaOH. Second, determine the strength of the standard HNO_3 in terms of phosphorus by titrating 0.5 gram of pure yellow ammonium phosphomolybdate by the above method. The phosphomolybdate should be dried for 1 hour at 100° C. before use.

CALCULATION.—$\text{P factor} = \frac{0.00825}{\text{cc. of } HNO_3 \text{ used}}$.

The standard ammonium phosphomolybdate may be prepared as follows: Acidify a dilute solution of Na_2HPO_4 with HNO_3, add an excess of MoO_3 solution, filter, wash the precipitate thoroughly with hot water, dry at 150° C. and keep in a glass-

stoppered vial. Determine the content of phosphorus by the pyrophosphate method.* Pure ammonium phosphomolybdate contains 1.65% of phosphorus.

NOTES.—See under the Alternative Method below.

Phosphorus (Alternative Method).—Instead of titrating the yellow precipitate, filter it on a 9-cm. filter paper which has been previously dried and weighed in a glass-stoppered weighing bottle. Wash the precipitate at least 5 times with 2% HNO_3 to remove all Fe salts. Absorb with a blotter the excess of moisture from the paper and precipitate, and dry in the oven at 100° C. for 1 hour. Weigh the paper and contents in the weighing bottle. Using 2 grams of steel, the weight of precipitate in milligrams $\times 0.00825 \times 100$ = percentage of phosphorus.

NOTES.—(1) In neutralizing the ammoniacal solutions with HNO_3, the latter should be added until the solution is straw color, otherwise a small amount of iron may later separate causing high results.

(2) It is essential that the yellow precipitate be washed with solutions of exactly the strength specified and until free from acid.

(3) When running a number of samples, the flask containing the filter paper and yellow precipitate must be kept tightly corked, and alkali should not be added until the remainder of the operation can be promptly carried through.

(4) When the alternative method of weighing the yellow precipitate is used, care must be observed that the filter paper is previously dried and weighed in a weighing bottle and that the final weight of filter and contents is made in exactly the same manner as the first weight of the filter.

Silicon.—Weigh 4 grams of steel into a 12-cm. casserole or evaporating dish and add 60 cc. of silicon mixture (see below). When effervescence ceases, rinse the sides of the dish with water and cover with a watch glass. Place on the hot plate and boil slowly but continuously to dryness. Bake to dehydrate the SiO_2, and cool. Take up with 75 cc. of dil. HCl (1 : 3) and bring to a boil. Keep at the boiling point until the solution is clear. Filter while hot through an 11-cm. filter, washing alternately with hot dil. HCl (1 : 1) and hot water until free from Fe; then wash the paper free from acid. Ignite in a platinum crucible and weigh as SiO_2. Calculate to Si. (If the precipitate is red, volatilize

* Dissolve a weighed amount of the yellow precipitate in NH_4OH and precipitate with an excess of magnesia mixture. Filter, ignite and weigh as $Mg_2P_2O_7$ (see p. 766).

with HF, evaporate to dryness, ignite and weigh again. The loss in weight is SiO_2.)

CALCULATION.—$SiO_2 \times 0.4672 = Si$.

Silicon Mixture.—Into 1500 cc. of water pour 500 cc. of conc. HNO_3, and then 150 cc. of conc. H_2SO_4.

CAUTION.—Mix in the above order, adding the H_2SO_4 very slowly, and let cool before shaking.

Sulfur.—There are two methods for sulfur in common use. The Gravimetric Method depends upon the oxidation of the sulfur to sulfate and precipitation and weighing as $BaSO_4$. The Evolution Method depends upon evolving the sulfur as H_2S, absorbing the latter and titrating it. On all steels for analysis in this laboratory the Gravimetric Method is used unless the type and nature of the steel is sufficiently well known so that a standard steel of similar composition may be run with it by the Evolution Method.

GRAVIMETRIC METHOD.—Dissolve 5 grams of the sample in 75 cc. of aqua regia (1 part conc. HNO_3 : 3 parts conc. HCl) in a covered 250-cc. beaker, adding only a little aqua regia at a time until the violent action has ceased. Then add approximately 0.5 gram of anhydrous Na_2CO_3, evaporate to dryness and bake for 0.5 hour on the hot plate. Add 30 cc. of conc. HCl; repeat the evaporation and baking; again add 30 cc. of conc. HCl and evaporate to a syrupy consistency. Then add 5 cc. of conc. HCl, 10 cc. of water and approximately 5 grams of sulfur-free powdered zinc, 20- to 30-mesh. Heat on the steam bath until the iron is reduced to the ferrous condition, adding more acid if necessary. When the solution becomes practically colorless, the reduction is complete. Filter off the SiO_2 and undissolved Zn, wash with hot water, dilute the filtrate to 100 cc., and heat to boiling. While boiling add slowly, a drop at a time, 10 cc. of a hot 10% $BaCl_2$ solution. Let stand until the precipitate has settled completely, preferably overnight. (If the analysis is urgent, boil for 30 minutes and filter as soon as the precipitate settles clear.) Wash the $BaSO_4$ precipitate once or twice with cold 2% HCl solution and then with hot water until free from chlorides. Ignite in a weighed platinum crucible, cool and add 1 drop of dil. H_2SO_4 (1 : 1) and 1 cc. of HF. Evaporate to dryness on the edge of a hot plate;

finally ignite, cool in a desiccator and weigh as $BaSO_4$. Carry through a blank determination on the reagents and subtract any $BaSO_4$ obtained in this blank. Calculate to Sulfur.

CALCULATION.—$BaSO_4 \times 0.1373 = S$.

NOTE.—This method is essentially that of the United States Bureau of Standards, slightly modified as a result of experience in this laboratory.

EVOLUTION METHOD.—Weigh 5 grams of steel into a 500-cc. Florence flask provided with a double perforated stopper carrying a 2-bulb safety tube, extending below the surface of the liquid, and an exit tube for gas, the latter connected to a delivery tube extending to the bottom of a tall glass tumbler. Place 30 cc. of $CdCl_2$ solution in the tumbler and fill two-thirds with water. Add 100 cc. of dil. HCl (1 : 1) to the drillings in the flask. Place the flask over an Argand burner, heat gently at first, and, when the drillings are dissolved, boil until the steam drives the last trace of H_2S from the evolution flask. Disconnect the flask, add 2 cc. of starch indicator* and 30 cc. of conc. HCl to the solution in the tumbler, titrating at once with standard iodine solution to the appearance of a permanent blue. From the factor of the iodine solution calculate the percentage of S.

Solutions.—CADMIUM CHLORIDE SOLUTION: Dissolve 30 grams of $CdCl_2$ in 300 cc. of water and add this to 800 cc. of water and 1200 cc. of NH_4OH.

IODINE SOLUTION: Dissolve 4 grams of iodine and 8 grams of KI in a little water and make up to 1 liter.

Standardization.—Standardize the iodine solution against 10 cc. of 0.1 N sodium thiosulfate solution, very accurately pipetted out, and calculate the factor so that it will give percentage of S on a 5-gram sample.

CALCULATION.—1 cc. 0.1 N $Na_2S_2O_3 = 0.001603$ gram S.

$$\text{Then S factor} = \frac{1}{\text{cc. of iodine used}} \times 10 \times \frac{0.001603}{5} = \frac{0.003206}{\text{cc. of iodine used}}.$$

NOTES.—(1) Care must be taken to prevent drillings from sticking to the neck of the wet flask.

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* See page 12.

(2) When all H_2S has been driven over, the tube extending into the tumbler will become hot from condensed steam, and further heating should be avoided.

(3) In case of very coarse drillings, which dissolve slowly, considerable acid will be carried over and neutralize the NH_3 in the $CdCl_2$ solution. In such cases care must be taken to keep the solution up to its original strength in NH_3. If such samples are encountered it is preferable to use the Elliott Method as described on page 163.

References.—Blair: "The Chemical Analysis of Iron"; Lord and Demorest: "Metallurgical Analysis."

QUALITATIVE ANALYSIS OF ALLOY STEELS

General.—This method covers qualitative tests for the detection in alloy steels of chromium, nickel, copper, cobalt, titanium, tungsten, molybdenum, and vanadium.

Preliminary Tests.—Dissolve 1 gram of the sample in 50 cc. of dil. HCl (1 : 1). An *immediate* blue color on the addition of HCl indicates Co. After all action ceases Cr, Ni, Cu, Co, and Ti are in solution, whereas W, Mo and V remain insoluble as a black residue. After this residue has settled, a green-colored solution indicates Ni or Cr. If a black insoluble residue remains, add 0.5 gram of $NaClO_3$ and boil the solution for 5 minutes. If the black residue changes to a lemon color, W is indicated. If the residue completely dissolves, the absence of W and the presence of Mo and V are indicated.

After filtering off the WO_3, if the residue did not dissolve, treat the solution with 20 cc. of dil. H_2SO_4 (1 : 1) and evaporate until SO_3 fumes are evolved. Treat the evaporated residue with 50 cc, of water and heat gently until the salts are dissolved. Use the resulting solution to confirm the presence or absence of Cu, Mo. V and Ti.

Confirmatory Tests.—*Molybdenum.**—Dilute the above solution to 200 cc. and nearly neutralize with NH_4OH. Then saturate with H_2S and boil until the precipitated sulfides of Mo and Cu coagulate. Remove this precipitate by filtration, wash and ignite at a very low heat. Treat the oxides of Mo and Cu in the crucible with 10% NaOH solution. The MoO_3 is thus dissolved while the CuO remains insoluble. Filter and test the filtrate for Mo by one of the following procedures:

* See also p. 157.

(1) Acidify the filtrate slightly with dil. HCl (1:1) and add 1 cc. of 5% $SnCl_2$ solution. Next add a few crystals of KCNS, whereupon the solution will assume a red color which will not fade if Mo is present.

(2) Acidify the filtrate with dil. H_2SO_4 (1:1) and saturate with H_2S. A dark brown precipitate indicates the presence of Mo. In case a dark brown precipitate is obtained, filter, ignite and treat with dil. H_2SO_4 (1:1) and metallic Zn. If Mo is present, the solution will first be colored blue, then green, and finally brown.

Copper.—Dissolve in HNO_3 the insoluble black residue from the NaOH solution and dilute with water. Add an excess of NH_4OH. If a blue color is obtained, the presence of Cu is indicated.

*Vanadium and Titanium.**—Concentrate the filtrate from the sulfides of Mo and Cu to approximately 100 cc. and add a slight excess of $KMnO_4$ solution. Next boil this solution for a few minutes and cool to room temperature. Add 10 cc. of *fresh* H_2O_2 and dilute to 100 cc., dividing into two equal portions. If Ti alone is present, the solutions are colored yellow. If V alone is present, the solutions are colored a deep brown. If both are present, the brown color due to the presence of V is readily distinguished. To detect Ti in the presence of V add 1 drop of HF to one solution, whereby the yellow color due to Ti will be destroyed. Then compare this solution with the solution to which no HF has been added and if a change of color is observed, Ti is indicated.

Tungsten.—The preliminary tests previously described will show whether W is present.

Chromium.—For the detection of Cr, Ni and Co in the presence of W, weigh another 1-gram sample into a 250-cc. beaker. Add 100 cc. of dil. HCl (1:1) and boil until all action ceases. The volume should be about 50 cc. Add an equal volume of water containing 0.5 gram of $NaClO_3$ and boil for 5 minutes. The W is converted to yellow WO_3, which is filtered out and discarded.

Inasmuch as the presence of too much Fe interferes somewhat with the delicacy of these tests, it is advisable to remove the excess from the filtrate by means of an ether separation which is carried out as follows:

* See also p. 153.

Add 3 cc. of dil. HNO_3 (1:1) and rapidly evaporate to about 40 cc. Cool to room temperature and transfer to a separatory funnel with the least possible amount of dil. HCl (1:1). The volume should not exceed 50 cc. Add 30 cc. of ether and shake well. The lower layer will contain only a small amount of Fe and Mo, but all the other elements. Run this lower layer into a beaker. Heat the solution gently on a steam bath to expel traces of ether, and add 20 cc. of dil. H_2SO_4 (1:1.) Evaporate until SO_3 fumes are evolved. Cool and add 50 cc. of water. When the separated salts have dissolved, remove any Cu or Mo which may be present by precipitation with H_2S. Filter the precipitated sulfides and boil the filtrate to expel excess of H_2S.

Divide the solution into 2 parts. To half of the solution add $\frac{1}{4}$ its volume of conc. HNO_3, followed by an excess of a concentrated solution of $KMnO_4$, and boil for 10 minutes. If, after settling, the solution is colored yellow, Cr is indicated. The boiling must be sufficiently vigorous, however, to decompose all of the excess of $KMnO_4$, forming a precipitate of MnO_2.

Test the solution further for Cr by transferring 20 cc. to a test-tube containing 5 cc. of *fresh* H_2O_2. The yellow chromate solution will change to blue and if shaken with further portions of ether, the latter will extract the Cr compound and will itself be colored blue.

Nickel.—Treat the remaining half of the above solution with 5 grams of citric acid. Make strongly alkaline with NH_4OH and saturate with H_2S. This will precipitate sulfides of Co, Ni, Fe and Mn. Filter, and carefully ignite the precipitate in a platinum crucible. Transfer the contents of the crucible to a beaker and dissolve in dil. HCl (1:1). Make the solution slightly ammoniacal and add about 0.5 gram of ammonium persulfate. Boil and filter to remove oxides of Fe and Mn.

Divide the filtrate containing Ni and Co into 2 portions. To one portion add 5 cc. of a 1% alcoholic solution of dimethylglyoxime. A bright red precipitate indicates the presence of Ni.

NOTE.—A rapid and convenient test to determine whether or not a steel contains nickel is as follows: Mix 1 volume of a 1% solution of dimethylglyoxime in alcohol with 4 volumes of 50% H_3PO_4. Apply a small amount of this mixture to the clean, bright surface of the steel and then add to it 2 or 3 drops of a 60% KOH solution. If Ni is present, a bright red coloration will be produced.

Cobalt.—Acidify the other portion of the persulfate solution slightly with dil. HCl (1:1) and heat to boiling. Add a freshly prepared solution of nitroso-beta-naphthol, which is made by dissolving about 0.5 gram of the reagent in 10 cc. of hot 75% acetic acid. Boil the contents of the beaker for a few minutes. Co, if present, will be precipitated as a red-colored compound together with some excess of the reagent. Filter the solution while hot and ignite the precipitate in a porcelain crucible to convert any Co to the oxide. Treat the residue with dil. HCl (1:1). A blue solution will be obtained, if Co is present. To confirm, make the solution ammoniacal, whereupon it will be colored pink, if Co is present.

Reference.—Methods of the Chemists of the U. S. Steel Corporation for the Sampling and Analysis of Alloy Steels, published in 1921 by J. M. Camp, Chairman of Chemists' Committee.

QUANTITATIVE ANALYSIS OF ALLOY STEEL

General.—This method covers the quantitative analysis of alloy carbon steels, *i.e.*, those containing, in addition to C, Mn, P, Si, and S, one or more of the following: Cu, Ni, Cr, V, W, Mo and Ti.

Sampling.—The points to be observed in sampling alloy steels for analysis are the same as those mentioned under Carbon Steel on page 133.

Total Carbon.—Use the procedure for Carbon Steel, page 134, omitting Note 1.

Manganese.—*Bismuthate Method for Ordinary Alloy Steels.*—Dissolve 1 gram of steel in 60 cc. of dil. HCl (1 : 1). When solution is complete add HNO_3, drop by drop, to oxidize the Fe. Add an equal volume of water and boil 10 minutes. Filter and wash any WO_3 with dil. HCl (1 : 7). Displace all HCl in the filtrate with HNO_3 by evaporating nearly but not quite to dryness, removing the last traces with $AgNO_3$. Then add 75 cc. of dil. HNO_3 (1 : 3). Cool and proceed according to the Bismuthate Method for Manganese in Carbon Steel (p. 136), titrating with standard sodium arsenite solution as there described.

Method for High-Chrome Steels.—In case the Cr content of the steel is over 2%, proceed as follows: Dissolve 1 gram of steel in 60 cc. of dil. HCl (1 : 1). Proceed as in the Bismuthate Method above described until the last trace of HCl has been replaced by

HNO_3 by evaporation. Add 100 cc. of colorless conc. HNO_3, set on the hot plate and heat to incipient boiling. Then drop in powdered $NaClO_3$ or $KClO_3$, a little at a time, adding each portion when the effervescence produced by the preceding portion has ceased. By the time 2–2.5 grams have been added the MnO_2 will have separated as a fine brown powder. Add 0.5 gram more of chlorate and boil gently for 10 minutes. If any SiO_2 is present in the solution after 3 or 4 minutes' boiling, add a few drops of pure HF. Then add 1 gram more of the chlorate and 25 cc. of conc. HNO_3 and boil for 10 minutes longer. Remove from the plate and cool by setting the beaker in water. When the MnO_2 has settled, filter without dilution through a Gooch crucible with a removable bottom and asbestos mat. Finally transfer the MnO_2 to the filter and wash the beaker and filter mat with colorless* conc. HNO_3 three or four times, or until the filtrate is colorless. This can be done without using more than 15–20 cc., by adding only a little each time and letting each portion run through before adding the next. Finally wash with a little cold water.

After washing the MnO_2 with cold water till free from acid (letting each successive portion of water run entirely through before adding the next, so as not to use in all more than 20 cc.), wash the asbestos and precipitate back into the beaker, which always has some MnO_2 adhering to it. Add standard ferrous ammonium sulfate solution (see note) from a burette, 5 cc. at a time, until after stirring and warming the MnO_2 is *completely* dissolved. Break up with a glass rod all lumps of asbestos and precipitate. Add a little water and run in standard $KMnO_4$ solution (see note) till the pink color remains permanent for 2 or 3 minutes. Read the burette and deduct the amount of $KMnO_4$ from its equivalent of ferrous ammonium sulfate solution. The difference is the amount of standard $KMnO_4$ solution equivalent to the Mn present in the precipitate. Multiply this difference by the Mn factor of the $KMnO_4$ solution and calculate to percentage.

NOTE.—The standard ferrous ammonium sulfate and standard $KMnO_4$ solution, described under the determination of Manganese in the method for

* If the HNO_3 is colored by lower oxides of N (from standing and the action of light), it can be purified by blowing a strong current of air through it until colorless.

Carbon Steel (p. 137), should be used for this titration. The Mn factor is not the same, however, as when the bismuthate method is used. In the bismuthate method the following reaction takes place:

$$10FeSO_4+2KMnO_4+8H_2SO_4=5Fe_2(SO_4)_3+K_2SO_4+2MnSO_4+8H_2O.$$

In the above reaction 1 Mn is equivalent to 5 Fe and the Mn factor may be calculated from the Fe factor of the $KMnO_4$ by the following equation:

$$\text{Mn factor}=\text{Fe factor}\times\frac{54.93}{279.20}$$
$$=\text{Fe factor}\times 0.1967.$$

When the MnO_2 is titrated in the method above described, however, the following reaction takes place:

$$MnO_2+2FeSO_4+2H_2SO_4=MnSO_4+Fe_2(SO_4)_3+2H_2O.$$

In this reaction 1 Mn is equivalent to 2 Fe and the Mn factor may be calculated from the Fe factor of the $KMnO_4$ by the following equation:

$$\text{Mn factor}=\text{Fe factor}\times\frac{54.93}{111.68}$$
$$=\text{Fe factor}\times 0.4919.$$

Phosphorus.—Dissolve 2–5 grams of steel in dil. HNO_3 (1 : 3) in a porcelain dish, evaporate to dryness and ignite to dull red; cool, dissolve in dil. HCl (1 : 1), filter and convert to nitrate by evaporating *nearly* to dryness with HNO_3 several times. Proceed as under Phosphorus in Carbon Steel (p. 133).

Silicon.—In alloy steels containing no tungsten determine Si as in Carbon Steel, page 140.

Notes.—(1) Silicious residues are likely to be contaminated with Ti and Al and should be evaporated with HF and H_2SO_4.

(2) When W is present, the WO_3 and SiO_2 are weighed together and separated as described later under Tungsten (p. 156).

Sulfur.—As in the case of ordinary carbon steels, there are two general methods for the determination of sulfur in alloy steels. The Evolution Method is much shorter and is generally applicable to the usual alloy steels. The Gravimetric Method is considered the more reliable, however, and should be used on all except routine samples whose general composition is known in advance.

Gravimetric Method.—Follow the procedure described under the Gravimetric Method on page 141. Any tungsten will separate as WO_3 and be filtered off with the SiO_2 and Zn.

Evolution Method.—Weigh 5 grams of drillings into the evolution flask described in the Evolution Method for sulfur on page 142. Assemble the apparatus as there described except that a 10-inch test-tube is inserted between the evolution flask and the tumbler containing the ammoniacal $CdCl_2$ solution. Fit the test-tube with a 2-hole rubber stopper. Through one hole insert a glass tube leading from the flask nearly to the bottom of the tube; through the other hole insert a glass tube bent with two right angles, one arm projecting just below the stopper on the inside and the other arm leading into the tumbler containing the $CdCl_2$ solution. For each determination place 20 cc. of water in the test-tube.

Carry out the manipulation exactly as described on page 142 except that conc. HCl is used in place of the dil. HCl (1:1). Take special precaution not to distill over an undue amount of HCl. When the usual titration of the contents of the tumbler is completed, add the contents of the test-tube and continue the titration until a blue color is obtained.

Copper.—Dissolve 5 grams of the sample in a mixture of 150 cc. of water and 12 cc. of conc. H_2SO_4. Dilute to about 500 cc. with hot water, heat to boiling and add 3 grams of sodium thiosulfate dissolved in 10 cc. of hot water. Boil a few minutes, let the precipitate settle, filter and wash with hot water. Dry the precipitate (which besides the CuS may contain graphite, silica, etc.), transfer to a small beaker, burn the filter and add the ash to the main portion. Digest the whole with aqua regia, dilute with hot water, filter, wash, add a few drops of H_2SO_4, evaporate to fumes of SO_3, cool, dissolve in water, add 15 cc. of conc. HNO_3, dilute to about 250 cc. and determine the Cu by electrolysis (see p. 182).

Notes.—(1) In the case of a steel insoluble in acid or containing tungsten, treat as described for Manganese (Bismuthate Method) and filter off the WO_3. To this filtrate add 12 cc. of conc. H_2SO_4, evaporate to fumes of SO_3, dilute to 500 cc. with hot water and proceed as described above, beginning "heat to boiling and add 3 grams of sodium thiosulfate."

(2) Instead of determining the Cu by electrolysis, it may be determined as CuO. Dilute the sulfate solution, obtained by any of the methods mentioned above, with water to about 50 cc., add an excess of NH_4OH, filter, wash with ammoniacal water, and pass H_2S through the cold solution. Filter, and wash with H_2S water. Dissolve the sulfide in aqua regia in a small porcelain dish, evaporate nearly to dryness, dilute with hot water, heat

to boiling and add a slight excess of a dilute solution of NaOH or KOH. Filter on a small ashless filter, wash with hot water, dry, transfer the precipitate to a platinum crucible; burn the filter and add its ash to the precipitate; moisten the whole with HNO_3, and heat, very gently at first, increasing the heat slowly to redness. Cool, and weigh as CuO. Calculate to Cu.

CALCULATION.—$CuO \times 0.7989 = Cu$.

Nickel (Cyanide Method).—Dissolve 1 gram of steel drillings in a 400-cc. beaker with 20 cc. of dil. HCl (1:1). When action ceases, add 10 cc. of dil. HNO_3 (1:1). Boil until red fumes have been driven off, add 100 cc. of citric acid solution, dilute to 300 cc., and add with a pipette exactly 5 cc. of standard $AgNO_3$ solution. Now add just sufficient NH_4OH to destroy the cloudiness, then 2 cc. of KI solution, and titrate with standard KCN solution to the disappearance of turbidity. The end-point is easy for an experienced operator to detect, and is not reached as long as a drop, when striking the solution, produces a spot clearer than the liquid around it. As soon as the end-point is reached all turbidity will have disappeared.

The cyanide first reacts with the nickel, then attacks the iodide. If it is thought that the end-point is passed, add a measured amount of $AgNO_3$ until a turbidity just appears. It is best to have another beaker containing a solution to be titrated, and to which no $AgNO_3$ has been added, placed beside the one being titrated so as to have a clear solution of the same color for comparison. If the citric acid was dirty, the solutions will be cloudy and should be filtered before the $AgNO_3$ is added.

SOLUTIONS.—*Standard Silver Nitrate:* Dissolve 2.885 grams of $AgNO_3$ in water and dilute to 1 liter.

Potassium Iodide: Dissolve 50 grams of KI in 250 cc. of water.

Citric Acid: Dissolve 380 grams of $(NH_4)_2SO_4$ in a mixture of 270 cc. of conc. NH_4OH and 1430 cc. of water, and add 240 grams of citric acid.

NOTE.—In case $(NH_4)_2SO_4$ is not available the solution may be made as follows:

(*a*) Pour 166 cc. of conc. H_2SO_4 into 250 cc. of water.

(*b*) Pour 712 cc. of conc. NH_4OH into 880 cc. of water.

Pour (*a*) into (*b*) very carefully, as considerable heat is produced; then dissolve 240 grams of citric acid in the mixture.

Standard Cyanide: Dissolve 8.85 grams of pure KCN (or 9.03 grams of 98% KCN) and 10 grams of KOH in water and dilute to 2000 cc.

STANDARDIZATION.—Standardize the KCN solution against the standard 3.50% nickel-steel of the U. S. Bureau of Standards, following the same procedure as above, each cc. of the above solution being equivalent to approximately 0.10% of nickel. An additional titration must be made in order to obtain the relation between the $AgNO_3$ and the KCN solution. This is accomplished in the solution after titration for standardization by adding exactly 10 cc. of standard $AgNO_3$ to the solution and running in standard KCN to the disappearance of turbidity. One-half of the amount of KCN here required is to be subtracted from the amount used in each determination. *Example:* Suppose that 10 cc. of $AgNO_3$ required 5.2 cc. of KCN to destroy the turbidity and in the actual determination 5.6 cc. of KCN were required. Then $5.6 - 2.6^* = 3.0$ cc. KCN actually required by the sample to destroy turbidity. Hence

$$\frac{(3.0 \text{ cc.} \times \text{Ni Factor})}{(\text{wt. of sample})} \times 100 = \text{percentage of Ni.}$$

Assuming the standard steel contains exactly 3.50% Ni, then

$$\text{Ni factor} = \frac{0.0350}{(\text{cc. KCN required}) - (\text{cc. KCN equiv. to 5 cc. } AgNO_3)}.$$

NOTES.—(1) When 2% or more Cr is present, proceed exactly as described above except to add 200 cc. of the citric acid solution instead of 100 cc.

(2) The presence of sulfates is necessary to obtain a sharp end reaction. AgI is soluble in a large excess of NH_4OH, so care should be taken to have the solution only slightly alkaline with NH_4OH. It must, however, be alkaline.

(3) If the titrated solutions are allowed to remain in open beakers for some time, a white film forms on the surface. This does not interfere with the analysis.

(4) The $AgNO_3$ solution used should not be stronger than that indicated above, for when a strong solution is used, the AgI, instead of forming a turbid solution, settles out as a curdy precipitate, which does not readily react with the cyanide.

(5) Such elements as V, Cr, W, Mo or Mn do not interfere, even when present in large amounts in the sample. Copper, however, is titrated with KCN, but is usually present in negligible quantities. If its presence is sus-

*One-half of 5.2 cc.

pected, nickel should be determined by the dimethylglyoxime method below.

Nickel (Dimethylglyoxime Method).—Dissolve 1 gram of the sample in 25 cc. of dil. HCl (1 : 1). When solution is complete, add HNO_3, drop by drop, to oxidize the Fe. Add an equal volume of water and boil for 10 minutes. Filter into a 600-cc. beaker and wash with dil. HCl. Boil and add 10 grams of citric acid dissolved in 50 cc. of water. Dilute to approximately 300 cc., render slightly alkaline with NH_4OH, then add a slight excess of acetic acid and heat to boiling. Add about 20 cc. of dimethylglyoxime solution, or 5 times as much dimethylglyoxime as there is Ni present. Then add NH_4OH until the solution smells slightly of NH_3 or reacts alkaline. While still hot, filter on a weighed Gooch crucible, wash well, dry at 100–120° C. for 45 minutes and weigh as nickel glyoxime. Calculate to Ni.

CALCULATION.—Nickel glyoxime $\times 0.2032 =$ Ni.

Chromium.—Dissolve 1 gram of the steel in 20 cc. of dil. H_2SO_4 (1 : 3). When solution is complete, add dil. HNO_3 (1 : 3) drop by drop, until Fe is oxidized. (5 cc. are generally sufficient.) Boil to remove nitrous fumes and dilute to 150 cc. with hot water. Add to the boiling solution from a pipette a few drops at a time of strong $KMnO_4$ solution, boiling between each addition, until a permanent precipitate of MnO_2 is produced which does not disappear after 20 minutes' boiling. An excess over the amount necessary to do this should be avoided, as it will render reduction of the excess $KMnO_4$ to MnO_2 very difficult and necessitate prolonged boiling. Remove from the heat and let settle. If reduction of excess $KMnO_4$ to MnO_2 is complete, the precipitate will settle quickly, leaving a clear yellow supernatant liquid; if not complete, the precipitate will not settle quickly and will leave a pink or reddish supernatant liquid and must be boiled again. Filter the cold solution, preferably into a 500-cc. Erlenmeyer flask; add 5 cc. of syrupy H_3PO_4, and a known excess of ferrous ammonium sulfate, and titrate the excess with standard $KMnO_4$. Subtract the $KMnO_4$ required for the excess titration from the ferrous ammonium sulfate originally added (in terms of the $KMnO_4$) and calculate the difference to Cr.

The H_3PO_4 decolorizes ferric salts, giving a better end-point, and should be added to the $Fe(NH_4)_2(SO_4)_2$ solution when obtaining its relation to the $KMnO_4$ solution.

SOLUTIONS.—*Ferrous Ammonium Sulfate:* Dissolve 50 grams of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in 1900 cc. of water and add 100 cc. of conc. H_2SO_4.

Permanganate: Dissolve 1.58 grams of $KMnO_4$ in water and dilute to 1 liter.

STANDARDIZATION.—Titrate the $KMnO_4$ solution against 0.7021 gram of pure $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ dissolved in a mixture of 15 cc. of conc. H_2SO_4 and 150 cc. of water to obtain its Fe factor and calculate from this the Cr factor (also the vanadium factor if desired).

CALCULATION.—As 0.7021 gram of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ is equivalent to exactly 0.1 gram of Fe, therefore the amount of Fe equivalent to 1 cc. of the $KMnO_4 = \frac{0.1}{\text{cc. } KMnO_4 \text{ used}}$.

Since 1 Cr is equivalent to 3 Fe in this reaction, we have:

$$\text{Cr factor} = \text{Fe factor} \times \frac{52.01}{167.52}$$
$$= \text{Fe factor} \times 0.3105.$$

Vanadium.—*Qualitative Test.*—Dissolve about 0.5 gram of the sample in 10 cc. of dil. H_2SO_4 (1:3), heating until action ceases. Add 5 cc. of conc. HNO_3 and boil until no more red fumes are evolved. If tungsten is present, filter. Pour half of the solution into each of two 6-inch test-tubes. Then add to one tube 5 cc. of water and to the other 5 cc. of 3% H_2O_2 solution. If V is present, the tube to which the peroxide was added will be distinctly redder than the other, even if there be only a few hundredths of a per cent of V in the sample. If Ti, but no V, is present, the color will be a clear yellow. If a red color is produced, V is present and possibly Ti also. Add 0.05 N $FeSO_4$* solution, 1 cc. at a time, shaking after each addition, until the red color gradually fades. If Ti is present, the red will change to a clear yellow. If none is present, the red will gradually fade out without changing to yellow.

Quantitative Determination.—Dissolve 5 grams of drillings in 30 cc. of dil HCl (1:1) in a small covered beaker. When dissolved, add a few drops of HF, warm, and add gradually 1 or 2 cc. of HNO_3 to oxidize the Fe. Evaporate to about 10 cc. Cool and

* Ferrous ammonium sulfate may be used.

pour into a 150-cc. separatory funnel with a very short stem. Wash out the beaker with warm HCl (1:1), transferring all the solution to the funnel. To keep the volume small, use successive small portions of 5–6 cc. of acid in washing. The total volume of solution in the funnel should not exceed 40 cc. Cool the funnel and contents and cautiously add 45–50 cc. of ether, previously saturated with HCl. Stopper and shake vigorously for 5 minutes, keeping cool by holding under running water. Set the funnel in a rack and let stand until the ether separates and the line between the two layers is sharp. Then remove the stopper carefully and draw off the aqueous solution down to the stop-cock, being careful to empty the stem. Add 5–6 cc. of dil. HCl (1:1) to the ether in the funnel and shake again. Let separate as before, and draw off the acid, adding this to the first extract. It is desirable to use as little acid as possible in washing, as it removes some Fe from the ether and increases that to be subsequently removed from the aqueous solution.

During the whole operation the ether and the funnel should feel cool to the hand; if allowed to become too warm, vapor pressure may blow the stopper out. The aqueous solution contains some dissolved ether, a little $FeCl_3$ (which should not exceed 2% of that in the original solution) and the whole of the chlorides of V, Ni, Co, Mn, Al, and Cu. Evaporate this solution to dryness several times with a large excess of HCl to reduce vanadic acid to divanadyl chloride, according to the equation:

$$V_2O_5+6HCl=2VOCl_2+3H_2O+Cl_2.$$

Add 5 cc. of conc. H_2SO_4 and evaporate until all HCl is expelled and fumes of SO_3 appear. By this operation divanadyl sulfate is formed by the reaction:

$$2VOCl_2+2H_2SO_4=V_2O_2(SO_4)_2+4HCl.$$

Let cool and dilute to 200–300 cc. Warm to about 60° C. and titrate with standard $KMnO_4$ solution. The reaction is:

$$5V_2O_2(SO_4)_2+2KMnO_4+8H_2SO_4 = 5V_2O_2(SO_4)_3+K_2SO_4+2MnSO_4+8H_2O.$$

Comparing this with the reaction for titrating ferrous iron:

$$10FeSO_4+2KMnO_4+8H_2SO_4 = 5Fe_2(SO_4)_3+K_2SO_4+2MnSO_4+8H_2O,$$

we find 10V equivalent to 10Fe, and

$$V = 0.9126\ Fe.$$

Hence, the value of the permanganate solution in terms of Fe, multiplied by 0.9126, gives its value in terms of V.

NOTES.—(1) Small amounts of ferric salts do not interfere with the reaction, but when Cr is present to the extent of 2% or over, the color of the chrome salt masks the end reaction. The color of the divanadyl sulfate is pale blue, while that of the chromium sulfate is green. It is, therefore, impossible to tell from the color of the solution under the conditions whether the sample contains V or not, the discoloration of the permanganate solution being the only indication of its presence. In such case proceed as under Chromium and Vanadium below.

(2) Run a blank on the reagents along with the sample and deduct from the titration before calculating to V.

Chromium and Vanadium.—Dissolve 1 gram of steel in 50 cc. of water and 10 cc. of conc. H_2SO_4 in a 500-cc. beaker and proceed as described previously under Chromium until the solution is ready to titrate. Then add a standard ferrous ammonium sulfate solution until the solution loses all brown tints and assumes a practically colorless shade in plain vanadium steels or a green color in chrome steels. Then add a few more cc. to insure an excess. Now add standard $KMnO_4$ solution, slowly and with vigorous agitation of the solution, until a very faint pink is obtained that persists after 30 seconds' stirring. Should even as much as 5 or 6% of Cr be present, a practiced operator can easily detect the pink tints through the chrome green. If it is desired to know the Cr content, record the amounts of ferrous ammonium sulfate and $KMnO_4$ solutions used and calculate the Cr content as described previously under Chromium.

Next, *just destroy* the pink tinge with ferrous ammonium sulfate solution. The solution is now ready for the vanadium titration. Add 2 cc. of a 2% solution of potassium ferricyanide (always use the same amount) and drop in slowly, with constant stirring, standard ferrous ammonium sulfate until a drop produces a green color free from yellow tints. If much Cr is present, add ferrous ammonium sulfate until the green chromium color begins to darken. It is well to add from time to time during the titration a drop of the indicator and note if a green coloration is produced at the point where the drop mixes with the solution.

The Fe value of the ferrous ammonium sulfate multiplied by 0.9126 gives the amount of V present.

A blank must be run on a steel free from V but otherwise of similar composition. It is also best to run at the same time a V determination on a steel containing a known amount of V.

NOTES.—(1) The presence of Cr increases the blank. If Cu is present, it will precipitate out when ferricyanide is added. In such case, add ferricyanide before the MnO_2 is filtered off, and filter off the copper ferricyanide with the MnO_2. If a further precipitate is produced when ferricyanide is added for titration, run another determination, using double the amount of ferricyanide to precipitate the Cu. Nickel, if present, will also slowly precipitate with ferricyanide. Mo does not interfere. If the sample is a W steel, when it is dissolved it should be digested until the precipitated WO_3 is a bright yellow. Then add enough permanganate to cause the precipitate to become chocolate-colored by the MnO_2 formed.

(2) It is absolutely essential in V and Cr titrations, when coming back with permanganate, to add the latter until 3 drops give a faint pink which remains visible after 30 seconds' stirring. The ferrous ammonium sulfate should be added until 3 drops produce a distinct darkening of the green but not a blue. A better way for an analyst unfamiliar with the reaction is to add an excess of permanganate and titrate the excess with standard arsenite.

Tungsten.—If Si is also to be determined use Method I; otherwise use Method II.

Method I.—Weigh accurately 1 gram of drillings into a 250-cc. beaker, add 100 cc. of aqua regia (75 cc. of conc. HCl+25 cc. of conc. HNO_3), and, after violent action ceases, evaporate to dryness. Dissolve the residue by boiling with 20 cc. of dil. HCl (1:1) and a few drops of HNO_3. Dilute with 100 cc. of water and boil until the WO_3 precipitate is bright yellow. Filter and wash well with hot HCl (1:1) to remove all Fe. Ignite in a platinum crucible until all paper is burned off, but do not heat the WO_3 hotter than a dull red. Cool in a desiccator and weigh.

Add 3 drops of H_2SO_4 and 5 cc. of HF and evaporate off the acids under a good hood, finally driving off the H_2SO_4 by heating the crucible near the top. This evaporation must be carried out with extreme care to avoid loss by spattering. Heat to dull red and weigh. The loss in weight is SiO_2. Calculate to Si.

CALCULATION.—$SiO_2 \times 0.4672 = Si$.

The residue of WO_3 always contains some Fe_2O_3. To correct for this, fuse it with 5 grams of Na_2CO_3 and a few small crystals

of $NaNO_3$ until all WO_3 is dissolved. Cool the melt, dissolve with hot water and filter off the residue of Fe_2O_3. Wash well with hot water, ignite and weigh. Subtract the weight so obtained from the weight of the impure WO_3 after removing the SiO_2. The difference is the weight of the pure WO_3. Calculate to tungsten.

CALCULATION.—$WO_3 \times 0.7931 = W$.

NOTE.—If, when filtering the WO_3, some of the precipitate adheres to the sides of the beaker, wash the acid out of the beaker, then remove with a few cc. of NH_4OH, rinsing into the platinum crucible with a little water. Evaporate to dryness and then place the filter paper in this crucible to ignite.

Method II.—Treat 1 gram of drillings in a 400-cc. beaker with 50 cc. of dil. HCl (1:1) and digest until all action ceases. Add 100 cc. of water containing 0.5 gram of $NaClO_3$. Boil until the W is converted to WO_3 as indicated by a bright lemon color. Filter, wash and ignite as previously described. High speed steels do not usually contain enough Si to require an evaporation with HF. If it is suspected that the sample contains over 0.50% Si, this evaporation should be made after ignition of the WO_3. After weighing fuse the residue with anhydrous powdered Na_2CO_3 as previously described, take up the fusion with water, filter, wash, ignite and weigh again. The difference between the last two weights is WO_3. Calculate to W.

Molybdenum. *Qualitative Test.*—Dissolve 0.5 gram of drillings in 25 cc. of dil HCl (1:1). Add 2 grams of $KClO_3$ and if W is present, heat until the residue is bright yellow. Filter and add to the filtrate 10 grams of KOH dissolved in 10 cc. of water. Boil for several minutes. Filter and pour the solution into a large test-tube. Add HCl until crystals of KCl begin to form, then add a few grains of granulated tin and heat *just to* boiling. Cool and add 0.5 gram of KCNS. If Mo is present, a red color develops, the depth of color depending upon the amount present.

The precipitation with KOH is to separate out the Fe, which would also give a red color with KCNS. The solution must not be heated too long with the tin present, otherwise the delicacy of the test will be impaired. The test will indicate the presence of as little as 0.2% or less of Mo.

Quantitative Determination.—Place 2 grams of drillings in a 450-cc. beaker and cover with 50 cc. of conc. HCl. Heat to boiling and add conc. HNO_3, a few drops at a time until the

sample is in solution and the Fe is oxidized. Very little more HNO_3 should be added than necessary to oxidize the Fe. A black film of carbonaceous matter will remain. Evaporate to the beginning of pastiness, add 50 cc. of hot water and 10 cc. of HCl and boil a few minutes. The WO_3 separates, if present. Filter and wash with hot water acidulated with HCl. To the filtrate add a solution of NaOH, shaking the flask well during the addition, until most of the free acid is neutralized, but not until a darkening in color takes place.

Transfer the solution to a separatory funnel. Open the stopcock of the funnel so that the solution runs out in drops, and let the drops fall into a 500-cc. volumetric flask containing 150 cc. of a 6% solution of NaOH heated nearly to boiling. Shake the flask vigorously while the stream of drops is running in. This is important, as otherwise some Mo will be carried down with the $Fe(OH)_3$. Finally wash the funnel, running the rinsings into the NaOH solution. The Fe and most of the Cr are precipitated as hydroxides. A little Cr goes into the filtrate as chromate.

Dilute the solution in the flask to 500 cc., mix well and filter through a large paper, rejecting the first few cc. of filtrate. Transfer exactly 250 cc. of the filtrate to a 500-cc. beaker and add HCl until the solution is just acid to methyl orange; then add 4 cc. of conc. HCl in excess. Add a few drops of sulfurous acid to reduce the small amount of CrO_3 usually present, and boil. Add 40 cc. of NH_4 acetate, made by adding 30% acetic acid to conc. NH_4OH until the latter is neutralized. Now add 40 cc. of a 1% Pb acetate solution, stir well, filter through a close filter paper and wash well with hot water. Ignite in a porcelain crucible and weigh as $PbMoO_4$. Calculate to Mo.

CALCULATION.—$PbMoO_4 \times 0.2614 = Mo$.

NOTES.—(1) When the sample is dissolved and oxidized with HNO_3, a little molybdic acid may precipitate. This would appear with the WO_3 if any were present.

(2) The treatment with NaOH forms Na_2MoO_4 which is soluble, while the Fe separates as $Fe(OH)_3$. If the acid solution is not added slowly and with vigorous stirring, the $Fe(OH)_3$ will carry down with it some molybdic acid. Ammonium acetate is added to reduce the acidity, by dissociation.

(3) If much W is present, dissolve the WO_3 in NaOH solution, dilute to 50 cc., add conc. HCl until the solution is acid and then 20 cc. in excess, and evaporate the solution to 10 cc. Dilute to 50 cc. and boil. Filter off the WO_3 and add the filtrate to the main filtrate.

Titanium. *Qualitative Test.*—See Vanadium (Qualitative).

Quantitative Determination.—Add to 1 gram of the sample in a 500-cc. flask 40 cc. of dil. H_2SO_4 (1 : 3). Heat to boiling until no more action takes place. Disregard any residue. Dilute to 250 cc. and add NH_4OH until a slight precipitate forms; then add a few grams of $Na_2S_2O_3$ and a few drops of H_2SO_4, or enough to make the solution clear. Heat until all Fe is reduced, as shown by the absence of color when a drop is tested with KCNS; then add a solution containing 25 cc. of water, 15 cc. of conc. NH_4OH, and 10 grams of KCN. Heat to boiling for several minutes.

Prepare a filter by shaking two 9-cm. filter papers in a flask with water until well macerated and then pouring the pulp through a funnel containing a platinum cone. Place this funnel in a suction flask and pour the solution through, using suction. Filter the solution quickly to prevent oxidation of Fe and wash well with water. Burn the paper and contents in a platinum crucible until all paper is consumed; then add 4 grams of $KHSO_4$, which has been previously fused to remove water; heat to fusion, and maintain at bright red heat for several minutes. Cool, add water enough to half fill the crucible and 5 cc. of H_2SO_4, and heat until the cake is all dissolved. Cool, transfer to a Nessler tube or other color comparitor, dilute to 100 cc. and add 3 cc. of H_2O_2 (ordinary 3% solution). If Ti is present, a yellow color will immediately appear. To the other tube add 100 cc. of 5% H_2SO_4, 3 cc. of H_2O_2 and standard titanium sulfate solution a little at a time, shaking after each addition, until the color matches the color of the solution of the sample. The amount of Ti in the sample will then be the same as that added to the comparison tube.

Notes.—(1) H_2O_2 containing acetanilid or any other preservative should not be used. The pure 3% H_2O_2 solution is satisfactory.

(2) *Standard Titanium Solution:* Ignite pure TiO_2 at dull red heat to constant weight. Weigh 0.5 gram of the anhydrous powder in a platinum crucible with 5 grams of pure $KHSO_4$. Melt cautiously and keep at a low red heat for 5–10 minutes until the TiO_2 all dissolves and the liquid becomes clear. Partially cool the crucible and add 5 cc. of conc. H_2SO_4, then heat again till the mass liquifies. Cool, and put the crucible and contents in 200–300 cc. of water containing 5% of H_2SO_4. When the fusion is dissolved, wash and remove the crucible. The TiO_2 should dissolve to a clear solution. If any residue remains, filter it out, wash, ignite and weigh, and deduct it from the TiO_2 taken, using the difference in calculating the strength

of the solution. Finally, dilute the solution with 5% H_2SO_4 until 1 cc. contains 0.001 gram of Ti.

$$TiO_2 \times 0.6005 = Ti.$$

REFERENCES.—Lord and Demorest: "Metallurgical Analysis," 4th ed.; Blair: "Chemical Analysis of Iron"; Johnson: "Chemical Analysis of Special Steels"; "Methods of the Chemists of the United States Steel Corporation for Sampling and Analysis of Alloy Steels," 36–42 (1921).

PIG AND CAST IRON

General.—This method covers the usual determinations required on all classes and grades of pig, charcoal and cast iron.

Sampling.—The points to be observed in sampling iron for analysis are as follows:

(1) The sample should preferably be drillings taken without the application of water, oil or other lubricant, and should be free from sand, dirt or other foreign matter. A magnet must not be used in separating the iron from foreign matter on account of the danger of losing graphitic carbon which is non-magnetic.

(2) All samples should be ground uniformly in a hardened steel mortar.

(3) Drillings in the case of cast iron should represent the entire cross-section of material less than 1 inch thick. On material over 1 inch thick, the sample should be taken midway between the surface and the center.

(4) Drillings in the case of pig iron should be taken midway between the surface and the center.

Total Carbon.—Determine total carbon by the solution-combustion method. For the general arrangement of the combustion apparatus see Fig. 7, p. 134.

Dissolve 1 gram of the sample in 75 cc. of a solution of copper potassium chloride. Stir constantly with a mechanical stirrer until the sample is dissolved (see Note 1) or let stand overnight. Complete solution is shown by the disappearance of all Cu from the bottom of the beaker. Filter on a previously ignited asbestos mat in a loose-bottomed Gooch crucible. Wash 5 times with dil. HCl (1 : 10), then 5 times with water. Do not let air draw through the mat and residue during filtering and subsequent washing. Transfer the mat and contents to the combustion boat, being careful not to lose any of the carbon, and dry at 100° C.

Introduce the boat with the residue into the center of the combustion tube, which is maintained at 850-900° C. for this determination (also that of graphitic carbon). Admit oxygen at the approximate rate of 26 bubbles per 10 seconds, or 250 cc. every 10 minutes. As soon as the carbon begins to burn, there is at first a rapid evolution of gas, which quickly ceases. When the oxidation of the residue is completed, the oxygen begins to flow at normal speed again. Allow 30 minutes for oxidation of the carbon residue and sweeping of all CO_2 from the combustion tube into the absorption apparatus. Weigh the CO_2 formed and calculate to C.

CALCULATION.—$CO_2 \times 0.2727 = C$.

Copper Potassium Chloride Solution: Dissolve 900 grams of $2KCl \cdot CuCl_2 \cdot 2H_2O$ in 2700 cc. of water and add 215 cc. of conc. HCl. Filter the solution through glass wool and asbestos.

NOTES.—(1) We have found the rotating electrode a very convenient stirrer for getting the sample into solution. Of course no current should be passed when it is used for this purpose.

(2) This method cannot be used if the material is an alloy iron. In this case a portion of the sample passing a 20- but not a 30-mesh sieve must be mixed with 2 grams of litharge and the carbon determined by direct combustion at 1000° C. A blank must be carefully determined upon the litharge at the same temperature before using, and this blank deducted from the weight of CO_2 found.

(3) See also notes (2) to (6) inclusive, under Total Carbon in Carbon Steel (p. 135).

Graphitic Carbon.—Weigh 1 gram of the sample into a 200-cc. beaker and add 60 cc. of dil. HNO_3 (1 : 3). Heat on the steam bath until the iron is all dissolved. Filter on a loose-bottomed Gooch crucible through asbestos and wash with water; dil. HCl (1 : 1); water; NH_4OH (1%); water; HCl (1 : 1); water; and water, in the order indicated. Transfer the asbestos and contents to the combustion boat, heat until dry in the oven at 100° C. and determine carbon in the regular way.

Combined Carbon.—Combined C is the difference between total C and graphitic C.

In special cases the combined C may be determined colorimetrically as follows: Dissolve 0.2 gram of the sample in 6 cc. of dil. HNO_3 (1 : 3) in a small test-tube, filter, wash with the least possible amount of water, and compare the color of the

filtrate with that produced by a standard pig iron run in the same manner. The standard iron must not vary more than 0.1% in carbon from the unknown.

Manganese (Bismuthate Method).—Dissolve 1 gram of drillings in 25 cc. of dil. HNO_3 (1 : 3) in a small beaker. When dissolved, filter into a 200-cc. Erlenmeyer flask, wash with 30 cc. of dil. HNO_3 (1 : 3), cool the filtrate, add about 0.5 gram of Na bismuthate, boil until the pink color has disappeared and dissolve any precipitate of MnO_2 by adding a few drops of a saturated solution of $FeSO_4$ or of sodium thiosulfate. Then heat until all nitrous fumes have been driven off, cool to 60° F., add about 0.5 gram of Na bismuthate and shake the flask vigorously for a few minutes. Add 50 cc. of 3% HNO_3* and filter the solution into a suction flask through an extra-porous alundum thimble, taking care not to fill the thimble so full that any of the solution comes in contact with the rubber connection. Wash with 50–100 cc. of the same acid and finally with water. From here proceed as directed on page 137, using for the standardization an iron (not steel) of known manganese content.

Phosphorus.—Dissolve 1 gram of the sample in a 250-cc. beaker with 100 cc. of dil. HNO_3 (1 : 3). Add 5 cc. of saturated $KMnO_4$ solution and boil until the excess $KMnO_4$ is decomposed and the solution contains precipitated MnO_2. Add a few crystals of tartaric acid and boil until the solution clears, then a few minutes longer to drive off all nitrous fumes. Filter into a 500-cc. Erlenmeyer flask and wash the precipitate thoroughly with hot water. Add 15 cc. of conc. NH_4OH and proceed as described under Phosphorus in Carbon Steel on page 138.

Silicon.—Weigh 1 gram of the iron into a 12-cm. casserole or evaporating dish and add 60 cc. of silicon mixture (see Note 2). When effervescence ceases, rinse the sides of the dish with water and cover with a watch glass. Place on the hot plate and boil slowly but continuously until a white crust of $FeSO_4$ forms and SO_3 fumes appear. Remove the dish from the hot plate and cool. Dilute immediately with 75 cc. of dil. HCl (1 : 3) and bring to a boil. Keep at the boiling point until the solution is clear. Filter

* This acid is prepared by adding 60 cc. of conc. HNO_3 to 1940 cc. of water and then adding 3–4 grams of Na bismuthate and shaking. It should be allowed to stand overnight before using.

while hot through an 11-cm. filter, washing with hot dil. HCl (1 :1) and hot water alternately until SiO_2 and paper are free from iron. Then wash the paper free from acid; ignite strongly and weigh as SiO_2. Calculate to Si.

CALCULATION.—$SiO_2 \times 0.4672 = Si$.

NOTES.—(1) If the precipitate is red from undissolved Fe, volatilize with HF. Ignite and weigh again. The loss in weight is SiO_2. Calculate to Si.

(2) *Silicon Mixture.*—To 1500 cc. of water add 500 cc. of conc. HNO_3 and then 150 cc. of conc. H_2SO_4 with constant stirring.

Sulfur (Evolution Method).—Proceed as on page 142.

NOTE.—In the case of very coarse drillings which dissolve slowly, considerable acid may be carried over and neutralize the NH_3 in the $CdCl_2$ solution. In such cases care must be taken to keep the solution up to original strength in NH_3. If such samples are encountered, it is preferable to use the Elliott Method as described below.

Sulfur (Elliott Evolution Method).—Thoroughly mix 5 grams of the sample with 0.25 gram of pure, finely powdered, anhydrous

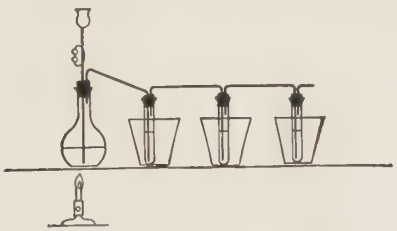


FIG. 8.—Apparatus for Sulfur in Iron. (Elliott Evolution Method.)

potassium ferrocyanide, and wrap in an 11-cm. filter paper. Place in a small porcelain crucible, cover and anneal at 750–850° C. for 20 minutes in a closed muffle. Cool slowly outside the muffle. The material *should be covered* practically completely by the charred paper, if the temperature has not been above 850° C. or if it has not been in the muffle too long. After cooling, crush the contents of the crucible slightly in a glass mortar and finally transfer to a 500-cc. Florence flask.

Connect the evolution flask with a condensing tube(1×8-in. test-tube) containing about 2 inches of water and standing in a conical beaker filled with cold water. A tube from this dips into a second test-tube containing 60 cc. of $CdCl_2$ solution, which agai

is connected with another test-tube containing more $CdCl_2$ (see Fig. 8).

Add 50 cc. of conc. HCl to the evolution flask and heat until the sample is in solution and all H_2S has been driven over. Disconnect the apparatus and wash the CdS into a tumbler. Add 3 cc. of starch solution and 15 cc. of conc. HCl and titrate at once with standard iodine solution to the appearance of a permanent blue.

SOLUTIONS.—*Cadmium Chloride Solution.*—Dissolve 20 grams of $CdCl_2$ in water with the aid of a few drops of HCl. Then add NH_4OH until the precipitate completely redissolves. Make slightly acid with acetic acid and then add 20 cc. excess. Dilute to 2 liters.

Standard Iodine Solution.—The same as used in the previous evolution method (p. 142).

STANDARDIZATION.—Standardize exactly as described under Sulfur in Carbon Steel (p. 142).

NOTE.—Copper, titanium, and vanadium are sometimes called for in this class of material. They may be detected and quantitatively determined as described in Blair, 7th ed., 184–185.

REFERENCES.—Blair: "Chemical Analysis of Iron." Lord and Demorest: "Metallurgical Analysis."

PIG-TIN AND TIN METAL

General.—The usual determinations required on pig-tin and tin metal are As, Sb, Bi, Cu, Fe, Pb and S. The sample should be in the form of either very fine drillings, millings, or sawdust—preferably the latter, as the accuracy of some of the determinations depends upon the fineness of the sample.

Arsenic.—Weigh 5 grams into a 300-cc. Erlenmeyer flask and digest with 50 cc. of conc. H_2SO_4 until completely decomposed. Cool the solution, dilute to 200 cc., and add 10 cc. of conc. HCl. Cool again and make faintly ammoniacal. Add 20 grams of oxalic acid crystals and agitate until solution is complete. Pass H_2S into the solution for 1 hour, let the precipitate settle, filter and wash with dil. H_2S water. Dissolve the sulfides of Sb and As through the filter paper into a 300-cc. Erlenmeyer flask with warm Na_2S solution. Add 15 cc. of conc. H_2SO_4 and approximately 3 grams of fused $KHSO_4$. Evaporate to copious fumes of SO_3. Add 50 cc. of water and 100 cc. of conc. HCl and warm

until the soluble salts are dissolved; then pass in H_2S for 1 hour. Filter the As_2S_3 on a filter paper which has been previously washed with dil. HCl (2 : 1) and wash the precipitate and the filter with acid of the same strength. Set aside the filtrate for the Sb determination.

Dissolve the As_2S_3 through the filter paper into a 250-cc. Erlenmeyer flask with warm Na_2S solution, add 10 cc. of conc. H_2SO_4 and approximately 3 grams of fused $KHSO_4$ and evaporate to fumes of SO_3. Dissolve the salts with 100 cc. of water and 5 cc. of conc. HCl, neutralize with NH_4OH and litmus paper, and make faintly acid with HCl. Cool and add $NaHCO_3$ cautiously, a little at a time, until the solution is alkaline. Then titrate with 0.1 N iodine and starch as described under Arsenic in Tin Ore, on page 171.

Antimony.—Dilute the above filtrate from the As_2S_3 to double its volume and precipitate the Sb by running a strong current of H_2S through the solution for about 15 minutes. Filter, dissolve through the filter paper with warm Na_2S solution and proceed as described under Antimony in Tin Ore, on page 172.

Lead.—Dissolve a 5-gram sample in a 400-cc. beaker on the steam bath by adding 40 cc. of conc. HCl and a few crystals of $KClO_3$, one at a time, until the solution becomes yellow. Then boil for 5 minutes, or until the excess of Cl is expelled. Cool and add strong NaOH solution slowly until the heavy white precipitate which is formed redissolves. Then add 50 cc. of strong Na_2S solution. Let stand in a warm place for 5 hours, filter and wash with dil. Na_2S solution. Dissolve the precipitate through the filter paper with hot dil. HNO_3 (1:1). Collect the solution in a 250-cc. beaker, add 15 cc. of conc. H_2SO_4, evaporate to fumes, cool, take up with 100 cc. of water and boil for a few minutes. Again cool, let settle, filter off the $PbSO_4$ and dissolve it with ammonium acetate solution, slightly acidified with acetic acid. Finally precipitate as $PbCrO_4$ as described under Lead in Tin Ore, page 170.

Iron.—Precipitate Cu and Bi in the filtrate from the $PbSO_4$ by passing H_2S through the solution for 1 hour. Filter, wash the sulfides well with dil. H_2S water and set aside the sulfides for determination of Cu and Bi. The Fe will be found in the filtrate from the CuS and Bi_2S_3. Add bromine to the solution

and boil to oxidize the iron completely. Boil off the excess of Br, add a slight excess of NH_4OH and boil until the odor of NH_3 is faint. Let settle, filter off the $Fe(OH)_3$ and wash with hot water. Ignite, cool in a desiccator and weigh.

Ordinarily, it is sufficiently accurate to assume that this ignited precipitate is pure Fe_2O_3. If, however, the Al content is desired or there is any reason for suspecting its presence, fuse the residue with $KHSO_4$, dissolve the melt in water, add sufficient H_2SO_4 to make a 5% solution, pass through a Jones reductor, and titrate the Fe with 0.1 N $KMnO_4$. Calculate to Fe_2O_3, subtract the latter from the weight of the combined oxides, and calculate the remainder to Al.

CALCULATIONS.—1 cc. 0.1 N $KMnO_4 = 0.007984$ gram Fe_2O_3.

$$Al_2O_3 \times 0.5291 = Al.$$

Bismuth and Copper.—Dissolve the CuS and Bi_2S_3 through the filter paper into a 250-cc. beaker with dil. HNO_3 (1:1). Precipitate the Bi with NH_4OH, filter and determine both the Bi and Cu as described under these elements on page 171.

Sulfur.—Weigh a 10-gram sample into an evolution sulfur flask and connect the apparatus in the same manner as in the determination of Sulfur in Steel by the Evolution Method, described on page 142. Instead, however, of using 100 cc. of dil. HCl (1 :1) as in the method for steel, use 100 cc. of conc. HCl and collect the liberated gas in 100 cc. of bromine water instead of in ammoniacal $CdCl_2$ solution. Boil until all H_2S has been driven over, then disconnect the apparatus, boil off the bromine and make the solution slightly ammoniacal and then slightly acid with HCl. Dilute to approximately 400 cc., bring to a boil and precipitate as $BaSO_4$ by adding, drop by drop, 15 cc. of a 10% $BaCl_2$ solution. Boil for 30 minutes after the addition, let settle till clear, filter, ignite, cool and weigh as $BaSO_4$. Calculate to S.

CALCULATION.—$BaSO_4 \times 0.1373 = S$.

TIN ORE

General.—Tin seldom exists in nature in the metallic state. Its ores occur both in veins and in alluvial deposits. Cassiterite (SnO_2), or tin-stone, is the most important ore and generally occurs in alluvial deposits. The color of the oxide may be black,

brown, reddish yellow, red, or brownish white. The streak is white to brownish. When pure the ore contains 78.77% Sn and its sp. gr. is 6.8—7.1. Another ore is Stannite (sp. gr. 4.3—4.52), a compound of Sn, S, Fe, Cu, and sometimes Zn.

The impurities most frequently associated with the oxide are pyrite, arsenopyrite, wolframite (tungstate of Fe and Mn), chalcopyrite, titaniferous iron, columbite, iron oxide, tourmaline, and sometimes blende and galena. To determine whether the mineral is SnO_2, fuse a finely ground portion in a porcelain crucible with three or four times its weight of NaCN and dissolve the mass in water. A tin globule, or globules, will be found if the material is SnO_2. The mineral may also be mixed with Na_2CO_3 and charcoal and fused on charcoal in a reducing flame.

When in veins the gangue generally consists of granite, slate, syenite, quartz or feldspar, and often carries garnets and zircons. Fluorspar is also frequently present, and by some authorities is considered a good indicator of tin-stone.

Portions of the deposit are often very rich, but the average ore, whether from veins or placers carries only 1–5% SnO_2. Most of the tin ores encountered along the Atlantic seaboard are concentrates and can be analyzed directly. Very low-grade ores, however, have to be concentrated before analysis, as later described (see p. 172).

The following procedures apply to high-grade ores or concentrates.

Preparation of Sample.—After a thoroughly representative sample has been obtained, grind it in an agate mortar until it passes a 200-mesh sieve. This is extremely important, as the accuracy of the analysis depends largely upon the fineness of the sample.

Tin.—Two methods are given below for the determination of tin. The Cyanide Method is considered the more accurate and is the method to be used in all cases of dispute or referee work. It is, however, a disagreeable method to handle and in cases where a large number of samples are to be analyzed, the Wet Method is preferable, although it should be checked up against a standard sample or against the cyanide method on one or more of the samples being tested. It requires considerable experience to obtain accurate results with the wet method.

Cyanide Method.—Treat 5 grams of the sample with 50 cc. of conc. HCl, boil for 15 minutes, add 10 cc. of conc. HNO_3 and boil for 10 minutes longer. This will remove all metallic impurities, such as Fe, etc. Filter, wash with warm NH_4OH, to remove any WO_3 which may be present, then with water, and dry the residue. Separate the residue from the paper as completely as possible, burn the paper and add this ash to the residue. Mix with 20 grams of finely divided NaCN (*Poison!*) and cover the mixture with 10 grams more of NaCN. Fuse in a Denver fireclay crucible for 20 minutes at a dull red, keeping the crucible covered during the fusion. (This must be done under a hood with a good draft to take away the poisonous fumes.) Cool under the hood without removing the cover, taking precautions when removing the crucible from the heat to agitate it as little as possible. After the melt is thoroughly cool, break the crucible, pound off the slag, wash the button thoroughly to remove the cyanide, dry and weigh.

The button may contain, besides metallic Sn, small amounts of Sb and other metals. It is therefore necessary to determine the amount of Sn in the button and calculate its percentage back to the original sample. For analysis of the button use the procedure described under Solder, on page 191.

Wet Method.—Weigh accurately 0.3 gram of the sample into a 15-cc. iron crucible and add approximately 3 grams of Na_2O_2* to the crucible, thoroughly mixing the ore and the peroxide with a glass stirring rod. Cover immediately with the iron crucible cover and place over a flame, using a *low* heat at first until the mixture is in a molten state, to avoid the possibility of explosion. Then increase the heat, and fuse until a quiet and complete melt is obtained. This usually requires about 15 minutes.

After the fusion is completed, cool, place in a beaker containing sufficient water to cover the crucible, and digest until the melt is completely dissolved from the crucible. Remove the crucible and cover, washing thoroughly. Add conc. HCl until the precipitated $Fe(OH)_3$ is dissolved. If the fusion has been effective, there should be no residue after acidifying, with the possible

* The Na_2O_2 must be fresh and in good condition; otherwise it will not be possible to fuse the ore and the analysis must be started again. If there is any question about the condition of the peroxide, open a new can.

exception of a little SiO_2, together with a small amount of scale which may come from the crucible. It is very easy to distinguish between the scale and undecomposed ore. If the ore has not been thoroughly decomposed, do not proceed any further, but start the analysis again.

Transfer the acid solution to a 500-cc. Erlenmeyer flask and add 500 cc. of conc. HCl. Place in the solution three pieces of sheet nickel* about 3×1 inches and 0.010 inch thick. Boil the solution for 1 hour, remove from the heat and cool under the tap, at the same time passing a strong current of CO_2 through the solution in order to eliminate the air as completely as possible. Run the CO_2 through the solution by means of a glass tube connected to the generator and fitted through one opening of a 2-hole stopper in the neck of the Erlenmeyer flask. When the solution is thoroughly cooled, run 5 cc. of starch solution through the second hole in the stopper, while the gas is still bubbling through the solution. Remove the tube, rinsing with water, and quickly insert another 1-hole stopper which has been cut off to fit the tip of a burette. Titrate the solution quickly with 0.1 N iodine by inserting the tip of the burette through the hole in the stopper. If air has access to the flask, the solution will be oxidized, giving low results. Calculate the titration to metallic Sn.

Calculation.—1 cc. 0.1 N Iodine = 0.005935 gram Sn.

Sulfur.—Weigh a 1-gram sample into a 250-cc. Erlenmeyer flask and add 15 cc. of conc. HNO_3 and a pinch of $KClO_3$. Cover the flask with a small watch glass and digest for 15–20 minutes. Remove the watch glass and evaporate to dryness. Take up with 15 cc. of conc. HCl and after the salts are in solution, dilute to 100 cc. Make ammoniacal, add 10 cc. of 10% $(NH_4)_2CO_3$ solution and boil. Filter, wash well and make the filtrate slightly acid with HCl, using litmus paper to avoid a large excess. Boil off all CO_2 and add 15 cc. of 10% $BaCl_2$ solution, drop by drop, to the boiling solution. Boil for 15 minutes, remove from the heat, let stand until clear (at least 1 hour), filter, wash with hot water, ignite and weigh as $BaSO_4$. Calculate to S.

Calculation.—$BaSO_4 \times 0.1373 = S$.

* This may be obtained in 6-inch strips from Eimer and Amend, New York City.

Iron.—Weigh a 1-gram sample into a 250-cc. Erlenmeyer flask, add 10 cc. of conc. HCl and 15 cc. of conc. HNO_3, evaporate to dryness and take up with 10 cc. of conc. HCl. Then dilute to 100 cc., filter, and wash thoroughly. Add a slight excess of NH_4OH to the filtrate, bring to boiling, let settle and filter. Dissolve the precipitate through the filter with hot 10% H_2SO_4. Add a little H_2O_2 to the solution. If the solution turns yellow, titanium is present. If no Ti is found, pass the warm iron solution through a Jones reductor and titrate with 0.1 N $KMnO_4$.

If Ti is present, evaporate the solution to fumes of SO_3, take up with 100 cc. of water and reduce the Fe by passing H_2S through the solution to saturation. Boil until the odor of H_2S is no longer noticeable and filter, if necessary, to remove sulfur. Cool and add 2 or 3 cc. of a saturated $HgCl_2$ solution to take care of the last trace of sulfide. Then titrate directly with 0.1 N $KMnO_4$. Calculate to Fe.

Calculation.—1 cc. 0.1 N $KMnO_4 = 0.005584$ gram Fe.

Silica.—Fuse 0.5 gram of the sample in an iron crucible with 5 grams of Na_2O_2 as described above under Tin (Wet Method). Digest the fusion with 100 cc. of water and add HCl until the solution clears. Evaporate to dryness and bake for 0.5 hour at 150° C. Take up with 100 cc. of dil. HCl (1:4), boil, filter, wash, ignite thoroughly in a weighed platinum crucible in the blast and weigh. Unless some of the scale comes off the iron crucible, it is safe to assume that this residue is true SiO_2 and an evaporation with HF will not be necessary. If any scale is mixed with the SiO_2, it will be necessary, after the first weighing, to evaporate with HF; then ignite and weigh again. Calculate the loss in weight by treatment with HF as SiO_2.

Lead.—Digest a 3-gram sample with 20 cc. of conc. HNO_3 until all brown fumes are expelled. Add 10 cc. of conc. HCl and digest 10 minutes longer. Cool, add 15 cc. of conc. H_2SO_4 and evaporate until white fumes of SO_3 are evolved. Cool, dilute to 100 cc. and boil to dissolve all soluble salts. Then cool, filter and wash with 10% H_2SO_4. The insoluble residue will contain not only the insoluble material in the ore, but precipitated $PbSO_4$. Dissolve this $PbSO_4$ by pouring several portions of hot ammonium acetate solution, slightly acidified with acetic acid, through the filter paper, collecting the solution in a 150-cc. flask. Wash

the insoluble material thoroughly with cold water, dilute the filtrate and washings to 300 cc., bring to a boil and add an excess of $K_2Cr_2O_7$ solution. Boil for 1–2 minutes, let settle, filter through a weighed Gooch crucible, wash with hot water and ignite gently on an asbestos mat or by placing the Gooch crucible in a larger platinum crucible. Weigh as $PbCrO_4$ and calculate to Pb.

CALCULATION.—$PbCrO_4 \times 0.6411 = Pb$.

Bismuth.—Warm the original filtrate from the $PbSO_4$ and insoluble material and pass H_2S into it for 1 hour. Filter and wash well with dil. H_2S water. Dissolve the precipitate through the filter with warm dil. HNO_3 (1:1), collecting the solution in a 250-cc. beaker. Wash the filter thoroughly. Make the filtrate slightly ammoniacal, bring to a boil, remove immediately from the heat and filter off the $Bi(OH)_3$. (Save the filtrate for the copper determination.) Dissolve the bismuth precipitate through the filter with warm dil. HCl (1:1) into a 600-cc. beaker, using as little acid as possible. Place litmus paper in the solution, make barely ammoniacal, then add 1 cc. of dil. HCl (1:1). If the neutralization with NH_4OH is carried out properly, this amount of HCl should make the solution distinctly acid.

Pour into the solution 400 cc. of boiling water. This will precipitate the Bi as BiOCl. Set aside in a warm place for an hour to allow the precipitate to settle. Filter through a weighed Gooch crucible, wash with cold water, dry at 105° C. for 4 hours and weigh as BiOCl. Calculate to metallic Bi.

CALCULATION.—$BiOCl \times 0.8024 = Bi$.

Copper.—Make the filtrate from the $Bi(OH)_3$ slightly acid with HCl and pass in H_2S for 15 minutes. Filter the precipitate of CuS, ignite in a weighed porcelain crucible, cool, add 2 cc. of conc. HNO_3 to the ignited residue, evaporate to dryness and ignite again. Weigh as CuO and calculate to Cu.

CALCULATION.—$CuO \times 0.7989 = Cu$.

Arsenic.—Weigh a 1-gram sample into a 250-cc. Erlenmeyer flask and add 30 cc. of conc. H_2SO_4 and 5 grams of fused $KHSO_4$, together with a piece of filter paper about an inch square. Heat until the solution is practically colorless. Cool and add 50 cc. of water and 100 cc. of conc. HCl. Warm to dissolve soluble salts and pass in H_2S for 1 hour. This precipitates the As but not the Sb. Filter off the arsenic sulfide, together with other insoluble

matter in the ore, through a filter paper which has been previously washed with dil. HCl (2 : 1). This treatment of the filter paper is necessary in order to avoid the precipitation of antimony in the paper. Wash the precipitate with dil. HCl (2 : 1) and set aside the filtrate for the Sb determination.

Dissolve the arsenic sulfide through the filter into a 500-cc. Erlenmeyer flask with warm Na_2S solution. After washing, add to the solution 10 cc. of conc. H_2SO_4 and approximately 3 grams of fused $KHSO_4$. Evaporate to fumes of SO_3. Cool, add 100 cc. of water and 5 cc. of conc. HCl and heat to dissolve soluble salts. Place a small piece of litmus paper in the solution, make slightly ammoniacal, then barely acid with HCl. Cool and add $NaHCO_3$ cautiously and in small portions until the solution is strongly alkaline. (A considerable excess gives a sharper end-point.) Add 5 cc. of starch solution and titrate with 0.1 N iodine to a blue color. Calculate to As.

CALCULATION.—1 cc. 0.1 N Iodine = 0.003748 gram As.

Antimony.—Dilute the original acid filtrate from the arsenic sulfide above to about double its volume and pass in a strong current of H_2S for 10 minutes. Let settle, filter off the antimony sulfide and wash with dil. H_2S water. Dissolve the sulfide through the filter into a 500-cc. Erlenmeyer flask with warm Na_2S solution. Wash well with water, add 10 cc. of conc. H_2SO_4 and approximately 3 grams of fused $KHSO_4$ to the solution and evaporate to fumes of SO_3. Cool, add 50 cc. of water and 10 cc. of conc. HCl and warm until soluble salts are dissolved. Now add 10 cc. more of conc. HCl and dilute to 200 cc. Cool and titrate with 0.1 N $KMnO_4$. The same permanganate solution may be used for this titration as is described under Antimony on page 193. It should be standardized against pure antimony.

REFERENCE.—The above procedures are essentially those submitted by the Eastern Metal and Refining Company. They have been thoroughly tried out in this laboratory and found to be reliable. The Wet Method for Tin, however, often gives trouble until the analyst becomes experienced with it. See also R. W. Lodge: "Notes on Assaying."

CONCENTRATION OF LOW-GRADE TIN ORE

General.—Owing to the high sp. gr. of SnO_2, it can be separated from the gangue materia. and some of the other impurities in its ores by washing and concentration. Wolframite unfortunatel-

has a specific gravity of 7.2–7.5, which is slightly higher than SnO_2 This necessitates subsequent purification when this mineral is present. If the tin ore carries much Fe_2O_3, this must be removed with acids, otherwise the resulting Sn will not collect in a button but will contain Fe and result in a porous, magnetic mass. Following are the steps in preparing a low-grade ore for assay or analysis:

(1) Concentration.
(2) Roasting concentrates.
(3) Panning concentrates and boiling in aqua regia.
(4) Panning concentrates again.

Concentration.—Weigh 500–1000 grams of ore, crushed to pass a 40-mesh sieve. If crushed too fine, the SnO_2 will slime badly, but it must be fine enough to liberate SnO_2 from the gangue. Carefully pan the ore again and again until no more concentrates can be obtained. This is done by placing the ore in a shallow pan, running a little water into the pan and shaking. Then carefully pour off the lighter constituents of the ore (tailings), allowing the heavy metallic compounds to settle to the bottom. *Do not pan too closely;* if a little gangue is left with the concentrates, it does no harm. Discard the waste matter or tailings.

Roasting.—Dry the concentrates (consisting of SnO_2, pyrite, and whatever heavy material happens to be in the ore, together with a small amount of gangue) and then place in a clay or iron roasting dish. Place this in a muffle, the bottom of which is hardly red, and heat slowly under a good hood. When the odor of SO_2 can no longer be detected, remove the dish, cool, and stir a little fine charcoal into the ore. This reduces sulfates, arsenates and antimoniates to lower forms and enables Sb and As to be set free, and is especially necessary when As is present. Roast again and repeat until a dead roast is obtained.* Everything in the concentrates should at this stage be in the form of oxides. It can now be panned to remove iron oxides and silica and then treated with acid, or treated with acid directly and then panned.

Treatment with Acid.—Boil the concentrates in aqua regia (1 part conc. HNO_3:3 parts conc. HCl) in which SnO_2 is insoluble. This removes practically everything except some SiO_2, TiO_2 and certain other compounds insoluble in aqua regia. If

* This point is reached when no more fumes of SO_2 or As_2O_5 are given off.

much SiO_2 is present, pan again. In some cases it is well to grind finely the tailings from this concentration and pan again. Dry the total concentrates, weigh and grind to pass an 80-mesh sieve.

The concentrates are now ready for assaying or analysis by the methods previously described. Results should be reported both on the basis of the concentrates and on the basis of the original ore.

ZINC (SPELTER)

General.—Spelter ordinarily used for brass and similar alloys is usually classified, according to the amounts of Pb and other impurities present, into four grades: A, "High Grade"; B, "Intermediate"; C, "Brass Special"; and D, "Selected." A fifth and still lower grade, "Prime Western," is principally used for galvanizing. These grades are covered by the standard specifications of the American Society for Testing Materials.

The methods of sampling and analysis described below are those generally accepted in the United States as standard in all the larger laboratories of both producers and consumers of zinc and zinc products. The methods of analysis are those originally proposed by Elliott and Storer and Price. Alternative methods are to be used only when apparatus or chemicals required in the preferred method are not available.

Sampling.—Select 10 slabs at random from a carload, saw each slab completely across from the middle of one long side to the middle of the other and use the sawdust for analysis. Or, drill three 9-mm. ($\frac{3}{8}$-inch) holes along one diagonal of each slab, boring completely through and taking care to make fine drillings. The holes should be drilled as nearly as possible at the middle and halfway between either end and the middle of such diagonals. Go over the drillings or sawings with a powerful magnet to take out any iron which may have come from the drill or saw, and mix the sample thoroughly. The drill or saw must be thoroughly cleaned before use, and no lubricant may be used in either drilling or sawing.

Lead (Electrolytic Method).—Place 8.643* grams of sample in a 400-cc. beaker and add sufficient water to cover. Then add

* An empirical factor weight 8.643 is used instead of the theoretical one (8.662) according to the American Society for Testing Materials: "Triennial Standards" (1918), and E. F. Smith's "Electro Analysis," 4th ed., 102.

gradually and cautiously 30 cc. of conc. HNO_3. When action is complete, boil the solution for a few minutes to expel nitrous fumes. Wash the watch glass and the sides of the beaker and transfer the solution to a 250-cc. beaker. Dilute to 200 cc. and electrolyze, using a rotating platinum cathode and a stationary platinum gauze anode, with a current of 5 amperes. The time required for electrolysis is from 30 to 45 minutes, depending upon the amount of Pb present. Test the solution for complete deposition of Pb by washing the watch glasses and sides of the beaker until the depth of the solution is increased about 0.5 inch. Then continue the current for 15 minutes, and if the newly exposed surface is still bright, the Pb is completely deposited. Wash the anode three or four times with water, once with alcohol and then dry in the oven, or on the hot plate, at 210° C. for 0.5 hour and weigh as PbO_2.

The weight of PbO_2 in milligrams, divided by 100, will give the percentage of Pb. The PbO_2 deposit can be readily removed by covering the anode with dil. HNO_3 and inserting a piece of Cu in the acid.

Lead (Alternative "Lead Acid" Method).—Place in a 350-cc. beaker 25, 15, 10 or 5 grams of drillings or sawings, according to whether the spelter is of Grade A, B, C, or D, respectively, and add, according to the size of sample taken, 300, 180, 120 or 60 cc. of "lead acid."* After all but about 1 gram of Zn is dissolved, filter on a close filter and wash out the beaker twice with "lead acid" from a wash bottle. Wash the undissolved matter from the filter into the original beaker with water and dissolve with a small amount of hot dil. HNO_3 (1 : 1). Add 40 cc. of "lead acid," and evaporate on the hot plate until strong fumes of SO_3 escape. When cool, add 35 cc. of water (which is the quantity

* "Lead acid" is a solution of 1 volume of H_2SO_4 in 7 volumes of water, saturated with $PbSO_4$. It is prepared as follows: Pour 300 cc. of conc. H_2SO_4 into 1800 cc. of water; dissolve 1 gram of lead acetate in 300 cc. of water and add to the hot solution with stirring. Let the solution settle for several days and siphon off through a thick asbestos filter for use. When "lead acid" is used, it is unnecessary to consider the solubility of $PbSO_4$, since the solution is always brought back to the same volume as the volume of "lead acid" originally added; consequently when the $PbSO_4$ is filtered, no more Pb remains in the filtrate than was originally added in the "lead acid."

of water evaporated from the "lead acid"), and heat to boiling. Add the first filtrate (containing the greater part of the Zn, and possibly a small amount of $PbSO_4$), stir well, and let stand for at least 5 hours, preferably overnight. Filter on a weighed Gooch crucible, wash with "lead acid," then with a mixture of equal parts of alcohol and water, and finally with alcohol alone. Set the Gooch crucible inside a porcelain crucible in order to avoid reduction of $PbSO_4$ by the flame gases and mechanical disintegration of the asbestos mat. Ignite for 5 minutes at the full heat of a Tirrill burner. Cool and weigh as $PbSO_4$. Calculate to Pb.

CALCULATION.—$PbSO_4 \times 0.6833 = Pb$.

Iron.—Place 25 grams of the sample in a tall 700-cc. beaker and dissolve cautiously in 125 cc. of conc. HNO_3. Boil, dilute to about 300 cc., add 10 grams of NH_4Cl and then NH_4OH until the precipitated $Zn(OH)_2$ has redissolved. Boil, let settle and filter on an 11-cm. S. & S. "Back Ribbon" or similar filter paper. Wash with dil. NH_4OH and with hot water. Dissolve the precipitated $Fe(OH)_3$ with hot dil. H_2SO_4 (1:4); wash with hot water; dilute the filtrate, if necessary, so that it will contain about 5% of H_2SO_4 and pass through the Jones reductor.* Wash first with 150 cc. of 5% H_2SO_4 and then with 100 cc. of water and titrate with $KMnO_4$ solution, containing approximately 0.2 gram per liter. 1 cc. of $KMnO_4$ solution will equal about 0.000334 gram of Fe. Run a blank with the same amounts of acid and water and correct accordingly.

Standardization.—Standardize the $KMnO_4$ against sodium oxalate furnished by the Bureau of Standards, using the following procedure: Weigh in duplicate 0.0200-gram portions of $Na_2C_2O_4$ into a 200-cc. Erlenmeyer flask, dissolve in 50–75 cc. of hot water (80–90° C.), and add 10 cc. of dil. H_2SO_4 (1:1). Titrate at once with the $KMnO_4$ solution, stirring vigorously and continuously. About 49–50 cc. of $KMnO_4$ solution will probably be required. The $KMnO_4$ must not be added more rapidly than 10–15 cc. per minute and the last 0.5–1 cc. must be added with particular care to allow each drop to be fully decolorized before the next is

* For manipulation of the Jones reductor see p. 186. If, before passing the solution through the reductor, a large amount of $PbSO_4$ is present, it is well to filter it off so as to prevent clogging the reductor.

added. The solution should not be below 60° C. at the time the end-point is reached. The use of a small thermometer as a stirring rod will be found convenient in this titration.

CALCULATION.—Fe factor $= \frac{0.01667}{\text{cc. of } KMnO_4 \text{ used}}$.

Cadmium.—Place 25 grams of drillings in a tall 500-cc. beaker; add 250 cc. of water and 55 cc. of conc. HCl and stir. When the action has almost ceased, add more acid with stirring, about 2 cc. at a time, and let stand after each addition of acid, until finally all but about 2 grams of Zn has been dissolved. About 60 cc. of acid in all are usually required. It is best to allow the first 55 cc. of acid to act overnight.

Filter, first transferring one of the undissolved pieces of zinc to the filter paper, and wash twice with water. Discard the filtrate. Wash the undissolved matter on the filter paper into a 500-cc. beaker; cover, and dissolve in HNO_3. Transfer to a casserole, add 20 cc. of dil. H_2SO_4 (1:1) and evaporate until fumes of SO_3 appear. Take up with about 100 cc. of water, boil, cool, and let stand until any $PbSO_4$ present settles completely. Filter off the $PbSO_4$, wash with water, retain the filtrate and discard the $PbSO_4$. Dilute the filtrate to 400 cc., add about 10 grams of NH_4Cl, and pass in H_2S for 1 hour. It is occasionally necessary to start precipitation of the CdS by the addition of a drop or two of NH_4OH to the dilute solution.

Let stand until the precipitate has settled, and then filter off the impure CdS in a loose-bottomed Gooch crucible. Remove the CdS by carefully punching out the bottom into a tall 200-cc. beaker. Wipe off any CdS remaining on the sides of the crucible, using a little asbestos pulp; add 60 cc. of dil. H_2SO_4 (1:5) and boil for 0.5 hour. In the case of spelters carrying large amounts of Cd, it may be necessary to add more acid. The dilute acid dissolves CdS and ZnS, but not PbS.

Filter and dilute to 300 cc.; add about 5 grams of NH_4Cl and precipitate with H_2S again, in order to get rid of traces of Zn. In case a large amount of Cd is present, a third precipitation may be necessary. After the final precipitation, let settle, filter and transfer to a weighed platinum dish; cover, and dissolve in dil. HCl (1:3). Also dissolve the sulfide remaining on the filter paper in hot HCl (1:3) and add it to the solution in the platinum dish.

Add a little H_2SO_4 and evaporate the solution on the hot plate until copious SO_3 fumes escape. Dilute with water, add a few cc. of conc. HNO_3 to oxidize any filter paper shreds, and again evaporate the solution until fumes of SO_3 come off freely. Remove the excess of H_2SO_4 by heating the dish cautiously, and finally heat to between 500° and 600° C., or to dull redness, cool and weigh as $CdSO_4$. Calculate to Cd.

CALCULATION.—$CdSO_4 \times 0.5392 = Cd$.

Cadmium (Alternative Method).—Proceed as above until the CdS has been dissolved in HCl. Oxidize with HNO_3 and filter from any sulfur. Transfer the solution to a 200-cc. beaker, add a drop or two of phenolphthalein and then pure NaOH or KOH solution until a permanent red color is obtained. Add a strong solution of pure KCN, with constant stirring, until the precipitate of $Cd(OH)_2$ is completely redissolved. Avoid using excess of KCN. Dilute the solution to 200 cc. and electrolyze with a current of 5 amperes, using a rotating platinum anode or cathode. (The Cd deposits on the cathode.) The time required is 1–2 hours. The solution should always be tested for Cd as follows: Raise the liquid in the beaker* and then note after 20 minutes the newly exposed surface of the electrode. If it is still bright, the Cd is completely deposited. Finally wash the electrode with water and then with alcohol. Dry at 100° C., cool, and weigh. The increase is metallic Cd.

REFERENCE.—Report of Subcommittee of Division of Industrial Chemists and Chemical Engineers, *J. Ind. Eng. Chem.* **7**, 547 (June, 1915).

ZINC DUST

General.—Commercial zinc dust is bought and sold upon its actual reducing power, which is measured by the amount of metallic Zn present or, as it is termed in the trade, "available zinc." The determination of the amount of available Zn, by means of $K_2Cr_2O_7$, and H_2SO_4, depends upon the following reaction:

$$3Zn + K_2Cr_2O_7 + 7H_2SO_4 = 3ZnSO_4 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O.$$

Standardization of Solution.—Prepare a solution of pure $K_2Cr_2O_7$ containing about 40 grams per liter. Pipette exactly

* As under Lead (Electrolytic Method), above.

10 cc. of this solution, with a certified pipette, into an Erlenmeyer flask. Add about 150 cc. of water, 3 cc. of conc. H_2SO_4 and 15 cc. of 10% KI solution. Titrate the liberated iodine with 0.1 N thiosulfate, adding a little starch indicator when the end-point has been nearly approached. The exact end-point is indicated by a change in color from dark brownish green to clear light green. This change is very sharp. Calculate the exact strength of the bichromate solution from the factor: 1 cc. 0.1 N thiosulfate $= 0.004903$ gram $K_2Cr_2O_7$.

NOTE.—It is possible to obtain $K_2Cr_2O_7$ sufficiently pure so that the solution does not need to be standardized.

Procedure.—Weigh accurately 1 gram of zinc dust into a 350-cc. beaker, add 50 cc. of standard $K_2Cr_2O_7$ solution and dilute with about 200 cc. of distilled water. Then add, drop by drop, *with constant stirring*, 20 cc. of dil. H_2SO_4 at the rate of 1 cc. per minute. It is very important that the liquid should be constantly stirred and no bubbles of hydrogen should escape. Finally, add 5 cc. of conc. H_2SO_4 and let stand until there is no further action. There will generally be more or less metallic Pb which will not be attacked. Heat just to boiling and then cool to room temperature. Transfer the liquid to a 500-cc. volumetric flask and dilute to the mark. Mix thoroughly and pipette 200 cc. into a beaker; add 15 cc. of 10% KI solution and titrate with 0.1 N thiosulfate as previously described. Calculate the amount of $K_2Cr_2O_7$ equivalent to the thiosulfate titration and multiply by 2.5. Subtract this from the total amount of $K_2Cr_2O_7$ in the 50 cc. originally taken and from the difference calculate the amount of metallic Zn.

CALCULATION.—$K_2Cr_2O_7 \times 0.6667 = Zn$.

REFERENCE.—Classen: "Ausgewählte Methoden der Analytischen Chemie," **1**, 353.

BRASS AND BRONZE

General.—This method covers the analysis of alloys of the brass or bronze type containing two or more of the following elements: Cu, Pb, Sn, Zn, P, Fe, Ni, Mn, As, Sb, and Al (the latter only in small amounts). It does not include white metals and aluminum alloys, containing considerable Al. The sample

for analysis should be in the shape of very fine drillings free from oil, iron dirt, or other foreign matter. If the composition of the alloy is unknown, a qualitative analysis should be made, using a 5-gram sample.

In those cases where an alternative method is given, the latter is to be used only when for some special reason the first method cannot be employed.

Phosphorus.—Dissolve 1 gram of the sample in 15 cc. of fuming HNO_3 and evaporate on the hot plate until most of the free acid is expelled. Add 10 cc. of conc. HCl and evaporate to dryness. Dissolve the residue in 10 cc. of HCl and 50 cc. of water, heat to boiling and precipitate the Pb, Sn, and Cu with granulated C. P. metallic Zn, 20-mesh. Use an excess of the Zn and let the reaction continue until no Pb, Sn, or Cu remains in the solution. Just before filtering add 5–10 cc. of conc. HCl to the solution. Filter immediately on a rapid filter, in the cone of which has been placed 1–2 grams of the zinc. Wash well with hot water and neutralize this solution (approximately 150 cc. in volume) with NH_4OH, adding the latter only until a permanent, heavy, curdy, white precipitate forms. Bring back again with conc. HNO_3, adding approximately 5 cc. in excess. Heat the solution to 70° C. and precipitate the phosphorus by adding 60 cc. of ammonium molybdate solution. Shake for 5 minutes and let the solution stand at least 0.5 hour, or until the yellow precipitate has completely settled. Filter through an 11-cm. filter paper, wash the precipitate five times with 2% HNO_3 then with 1% KNO_3 solution until *free from acid* (approximately 15 times).

Place the filter and contents in the original flask, which has been thoroughly rinsed with water, and add approximately 50 cc. of cool water and a measured amount of standard NaOH solution from a burette, 5 cc. at a time, sufficient to completely dissolve the yellow precipitate. Cork the flask and agitate violently until the filter paper is disintegrated; add 3 drops of 1% phenolphthalein solution with a medicine dropper, and titrate with standard HNO_3 to the disappearance of the pink color. The same standard acid and alkali may be used as employed for determining Phosphorus in Steel, as described on page 139.

CALCULATION.—Subtract the number of cc. of HNO_3 used from the number corresponding to the volume of NaOH added. The difference is the cc. of HNO_3 equivalent to the phosphorus in the sample, and this, multiplied by the value of the HNO_3 in terms of phosphorus, gives the weight of phosphorus in the sample.

Tin.—*If the alloy contains over 1.5% of Sn:* Weigh 1 gram into a 250-cc. beaker, add 15 cc. of dil. HNO_3 (2:1), cover immediately with a watch glass and, when violent action ceases, boil until no more red fumes are given off. Place the beaker on a water bath and digest for 0.5 hour. Dilute with 50 cc. of water and filter at once, if the alloy contains phosphorus, washing very thoroughly with 2% HNO_3.

Test the last drops of the filtrate with a little potassium ferrocyanide or ammonium sulfide solution; neither solution should give any precipitate. Place the filter paper and contents in a weighed *porcelain* crucible, smoke off the paper and ignite for 15 minutes in the full heat of a Tirrill burner. Cool in a desiccator and weigh. This represents $SnO_2+Sb_2O_4+P_2O_5$, together with traces of Fe, Cu and Pb. (Save these mixed oxides.) The P and Sb are separately determined, calculated to oxides and subtracted from the above weight. The remainder is SnO_2. Calculate to Sn.

CALCULATION.—$SnO_2 \times 0.7877 = Sn$.

If the alloy contains less than 1.5% of Sn: Dissolve 5 grams in 40 cc. of dil. HNO_3 (2:1) and treat as above described. In this case the filtrate should be made up to volume and an aliquot equivalent to 1 gram taken for the subsequent determinations of Cu, Pb and Zn.

NOTE.—In the case of brass or bronze containing less than 10% Sn and less than 0.7% P, no further purification of the mixed oxides is necessary; but if above these limits, the mixed oxides must be purified as follows: Fuse the ignited precipitate with a mixture of finely powdered sulfur and Na_2CO_3 in the proportion of 1 part of the precipitate to 3 parts each of S and of Na_2CO_3 in a covered porcelain crucible until the odor of SO_2 has disappeared. Cool and dissolve the fusion in hot water; add an excess of Na_2SO_3 to convert any polysulfides to monosulfides, filter and wash the precipitate thoroughly. This precipitate contains Cu, Pb, and Fe. Dissolve in dil. HNO_3 (1:3). Determine the Cu and Pb electrolytically and the Fe with NH_4OH in the regular way. Calculate the weights thus found to the oxides and subtract from the original precipitate.

CALCULATIONS.—

$$P \times 2.2892 = P_2O_5.$$
$$Sb \times 1.2628 = Sb_2O_4.$$
$$PbO_2 \times 0.9331 = PbO.$$
$$Fe \times 1.4298 = Fe_2O_3.$$
$$Cu \times 1.2517 = CuO.$$

Copper and Lead.—*When lead is 10% or less:* Dilute the filtrate from the Sn determination to approximately 200 cc. and add conc. HNO_3 until the solution contains approximately 10%. Then add 1 cc. of conc. H_2SO_4. Electrolyze the solution in a beaker, starting with a current of 2 amperes and gradually working up to 3 amperes, as the blue color of the solution disappears. Use either a rotating anode or a rotating cathode and continue the electrolysis for 45 minutes. At the end of this time stop the rotation of the electrode but do not turn off the electrolysis current. Lower the beaker and shut off the current just before the electrodes come out of the solution. Quickly wash the electrodes with a stream of distilled water from a wash bottle. Remove and immerse immediately in methyl alcohol. Then burn off the alcohol in the air, keeping the electrode in constant motion. Cool in a desiccator and weigh. The cathode contains the Cu in the metallic state and the anode contains the Pb as PbO_2. Calculate the latter to Pb.

Test the solution for complete removal of Cu and Pb by further electrolysis with fresh electrodes and weigh any further deposit which may form.

CALCULATION.—$PbO_2 \times 0.8643 = Pb.$*

NOTES.—(1) In case no Pb is present, the addition of 4 cc. of conc. H_2SO_4 before electrolyzing aids materially in getting a good Cu deposit.

(2) Extreme care must be exercised that the electrodes are completely dry before weighing. The alcohol should be changed frequently, as it soon absorbs water and drying becomes difficult.

(3) In case there is only a trace of Pb present, a separate 5-gram sample should be run for this element alone.

In the case of alloys containing more than 10% of Pb the PbO_2 is likely to flake off the anode and electrolysis is not a suitable method. Proceed therefore as follows:

To the filtrate from the Sn determination add 10 cc. of conc. H_2SO_4. Evaporate the solution until white fumes of SO_3 come off

* Empirical factor (p. 174).

freely. Then cool thoroughly and add 150 cc. of water; boil and let stand until perfectly cool. Filter the $PbSO_4$ on a weighed Gooch crucible, and wash with a 5% solution of H_2SO_4, and then with a mixture of equal parts of alcohol and water until the washings are free from acid. The alcohol should not be run into the main filtrate as it will interfere with the subsequent electrolysis for Cu. It is used merely to remove the acid of the first washing liquid.

Dry in the oven to remove alcohol and moisture, then set the Gooch crucible inside of a platinum crucible and ignite to a dull red heat. Cool in a desiccator and weigh as $PbSO_4$. Calculate to Pb.

CALCULATION.—$PbSO_4 \times 0.6833 = Pb$.

NOTE.—In case this procedure is followed, the Cu is determined by electrolysis of the filtrate as above described.

Zinc (Electrolytic Method).—To the filtrate* from the Cu and Pb determinations add 5 cc. (not more) of conc. H_2SO_4 and evaporate to the appearance of SO_3 fumes. Cool, rinse into a suitable beaker, and dilute to approximately 150 cc. Add 50 cc. of 30% NaOH solution and electrolyze the solution, using a current of 3 amperes and 2.5 volts, and a cathode which has been plated with Cu. The cathode used previously in the determination of Cu is suitable. The Zn generally deposits out in 15 minutes. After weighing the deposit, however, dissolve off the Zn in dil. HCl (1 : 1), wash, dry and weigh; then electrolyze for 10 minutes more in the same solution to insure the complete removal of all Zn. The manipulation for this determination is exactly as in the Cu determination and the Zn is weighed as metallic zinc.

NOTES.—(1) The amount of Zn weighed on the electrode should not be over 0.1 gram. If, therefore, the alloy contains more than 10% of Zn, dilute the filtrate from the Cu and Pb determinations to a suitable volume in a volumetric flask and take an aliquot that will yield not more than 0.1 gram of Zn.

(2) If Pb has been determined as $PbSO_4$ and 10 cc. of H_2SO_4 used, add 25 cc. more of the 30% NaOH solution to take care of the extra acid.

(3) Blanks should be run frequently on the NaOH to make sure that it contains no Zn. J. T. Baker's C. P. NaOH (electrolytic) has been found satisfactory.

* Or to an aliquot. (See Note 1.)

Zinc (Phosphate Method).—In the filtrate from the electrolysis of Cu and Pb precipitate the Fe and Al as hydroxides by the addition of an excess of NH_4OH. Filter and determine Zn in the filtrate as follows:

Add conc. HCl to the above solution until it is faintly acid, then add 2 cc. in excess. Now add an excess of a 10% solution of NH_4 or Na phosphate and heat to boiling. Add NH_4OH rapidly until all the precipitate redissolves. Bring back to acidity slowly with acetic acid and add 1 cc. excess. Stir briskly until the precipitate becomes crystalline, taking care that the policeman does not touch the sides of the beaker. Set the beaker aside for several hours, filter on a weighed Gooch crucible, wash with hot water, ignite strongly and weigh as $Zn_2P_2O_7$. Calculate to Zn.

CALCULATION.—$Zn_2P_2O_7 \times 0.4290 = Zn$.

Manganese (Bismuthate Method).—Dissolve 10 grams of the sample in 70 cc. of dil. HNO_3 (1 : 1), adding only a small amount of acid at a time to avoid loss by foaming. Evaporate to approximately half volume. Add 30–40 cc. of water, filter off any SnO_2 and wash the precipitate thoroughly with hot water. In case both Mn and Fe are desired, make up the solution to volume, retaining one-half for the determination of Fe and the remainder for the Mn determination. Most samples of so-called manganese bronze contain a very small amount of Mn, in which case take an aliquot representing 5 grams. In no case, however, should the aliquot taken for analysis contain over 0.015 gram of Mn. Remove the Cu and Pb by electrolysis and evaporate to 50–75 cc.; cool to tap-water temperature and add approximately 0.5 gram of sodium bismuthate. Let stand for several minutes with occasional shaking. Place an alundum filtering tube in a Gooch crucible holder, making the connection with rubber. Filter the solution through the alundum with suction. The alundum tube should fit well down into the glass crucible holder and the solution should at no time come within 0.5 inch of the place where the rubber connection is made on the outside of the tube. Titrate the filtered solution at once with standard sodium arsenite solution.

NOTE.—The arsenite solution is made to contain approximately 1 gram of As_2O_3 per liter. The solution described under Manganese in Steel on page 137, is satisfactory.

Manganese (Alternative Method).—In case the estimations of Sn and Mn only are desired, evaporate the filtrate from the Sn determination to small bulk in a 300-cc. Erlenmeyer flask. Add 50 cc. of conc. HNO_3 (which must be water-white) and bring to a boil. Add 2–3 grams of $KClO_3$, a few crystals at a time, and boil until the MnO_2 is completely precipitated and all nitrous fumes are driven off. Filter through an asbestos mat in a Gooch crucible and wash *free from acid* with hot water, allowing all HNO_3 to run through the filter before starting to wash with water. Transfer the asbestos and precipitate to the original flask and add a measured excess of standard ferrous ammonium sulfate solution, 5 cc. at a time. Agitate until the brown MnO_2 is dissolved. It may be necessary to break up some of the lumps with a stirring rod before solution is possible. Titrate the excess of ferrous iron to a pink color with standard $KMnO_4$. (The same standard ferrous ammonium sulfate and $KMnO_4$ solutions may be used as for the determination of Chromium in Steel, p. 153.) Deduct from the amount of ferrous ammonium sulfate used (expressed in terms of the $KMnO_4$ solution) the amount of $KMnO_4$ required for the back titration. The difference is the amount of standard $KMnO_4$ solution consumed by the Mn present in the precipitate. Calculate the Mn factor of the $KMnO_4$ solution by multiplying its Fe factor by 0.4919.

Iron.—Use a 5-gram aliquot of the filtrate from the Mn determination, or, in case this element is not determined, dissolve 5–10 grams of the finely divided sample in HNO_3, boil until nitrous fumes are expelled and dilute with 100 cc. of water. Filter off any metastannic acid and wash thoroughly with hot water. Add a small amount of NH_4Cl to the filtrate and an excess of NH_4OH sufficient to redissolve any white $Zn(OH)_2$ formed. Heat to boiling, filter and wash the precipitate with hot water until the washings are free from Cu. Dissolve in hot dil. HCl (1 : 1) and repeat the process. After the second precipitation, dissolve the $Fe(OH)_3$ by pouring hot dil. H_2SO_4 (1 : 4) through the filter paper, washing the filter thoroughly with the 1 : 4 acid and hot water. Dilute until the solution contains about 5% of H_2SO_4. Meanwhile prepare the Jones reductor (see note 2) as follows:

Connect the suction bottle with a vacuum pump, fill the reductor while the stop-cock is closed (or nearly so) with warm 5% H_2SO_4 and then open the stop-cock so that the acid runs through slowly. Continue to pour acid in until 200 cc. have passed through, then close the cock *while a small quantity of liquid is still left in the funnel.* Remove the filtrate and again pass through 100 cc. of warm 5% acid. Test this with 0.1 N $KMnO_4$ solution. A single drop should color it permanently; if it does not, repeat the washing. Be sure that no air enters the reductor. (If it is impossible to obtain an acid solution which does not color with 1 drop of $KMnO_4$ solution, the entire filtrate may be titrated and the titration applied as a negative blank correction in the determination.)

Pour the acid iron solution while hot (but not boiling) through the reductor at a rate not exceeding 50 cc. per minute. Wash out the beaker with 5% H_2SO_4 and follow the iron solution without interruption with 175 cc. of warm acid, and finally with 75 cc. of water, leaving the funnel partially filled. Remove the filter flask and cool the solution under the water tap. Add 10 cc. of dil. H_2SO_4 and titrate to a faint pink with 0.05 N $KMnO_4$ solution directly in the filter flask. Calculate the titration to Fe.

CALCULATION.—1 cc. 0.05 N $KMnO_4$ = 0.00279 gram Fe.

NOTES.—(1) If the alloy contains tin, the iron obtained from the purification of the SnO_2 precipitate must be added to that found in the main solution.

(2) The Jones reductor consists of a glass tube about 30 cm. long and 18 mm. inside diameter with a glass stop-cock at the bottom. In filling it, first place a platinum spiral or a few glass beads in the bottom and then a plug of glass wool followed by a thin layer of asbestos such as is used for Gooch crucibles. Finally fill the tube with amalgamated zinc to within about 5 cm. of the top and cover it with a little glass wool serving as a filter.

The *amalgamated zinc* may be prepared as follows: Dissolve 5 grams of mercury in 25 cc. of dil. HNO_3 (1 : 1), dilute to 250 cc. and transfer to a heavy liter flask. Add to the solution 50 grams of granulated zinc (20–30-mesh), shake the mixture thoroughly for 1–2 minutes and then pour off the solution and wash the zinc free from acid with distilled water.

Arsenic.—Weigh 3–10 grams of the sample (according to the As content) into a Kjeldahl flask; add a solution of $FeCl_3$ (made by dissolving 20 grams of Fe_2O_3 in 150 cc. of conc. HCl); and distill slowly, collecting the distillate in a liter Erlenmeyer flask. When the distillation is complete (after two-thirds of the solution

has distilled over) neutralize the distillate with stick NaOH or strong NaOH solution, acidify again with HCl and then make faintly alkaline with $NaHCO_3$ solution (the solution must be kept cool during this process). Add a few drops of starch solution, titrate with 0.01 N iodine solution and calculate to As.

Always run a blank distillation, using the same amount of reagents but omitting the sample, and subtract the titration obtained on the blank from that required by the sample.

The iodine solution must always be freshly standardized against pure As_2O_3 and the factor thus obtained.

Standard 0.01 N Iodine Solution.—Dissolve 1.27 grams of resublimed iodine and 2 grams of KI in 200 cc. of water in a casserole. When solution is complete, transfer to a volumetric flask and dilute to 1 liter. (Or, dilute 100 cc. of the laboratory stock solution of 0.1 N iodine to 1 liter.) Standardize the solution against C. P. As_2O_3 as follows:

Weigh out 0.1000 gram of As_2O_3 into a small beaker and dissolve in NaOH solution (2–3 grams of NaOH and 10 cc. of water). Dilute to 500 cc. in a volumetric flask with CO_2-free water. Acidify 50 cc. of this stock solution with 5 cc. of conc. HCl and then make slightly alkaline with $NaHCO_3$. Titrate with the iodine, using starch as an indicator. Calculate the arsenic factor of the solution.

$$\text{Calculation.—As factor} = \frac{0.007575}{\text{cc. of Iodine required}}.$$

Antimony.—Dissolve 5–10 grams of the sample in a 500-cc. Erlenmeyer flask in 30 cc. of conc. HNO_3. Add sufficient pure tin so that the ratio Sn : Sb is at least 3 : 1, otherwise the Sb will not be completely precipitated. Evaporate the solution to 10 cc. and then dilute with hot water to 250 cc. Boil for 15–20 minutes and then let the precipitate settle with the flask at an angle of 45°. The precipitate should settle out well. If it does, carefully decant as much of the solution as possible, but do not lose any of the precipitate. If the precipitate does not settle out well, decant through an asbestos mat in a Gooch crucible and then return the precipitate and asbestos to the flask. If much Cu is present, it is advisable to add more hot water and let settle; then decant again. The object is to get rid of most of the Cu

Add 15 cc. of conc. H_2SO_4 and 4–5 grams of K_2SO_4 to the flask and evaporate to white fumes. Do not drive off all free H_2SO_4 or the melt will become hard on cooling. Then add 0.5 gram of powdered tartaric acid. Heat strongly until the solution becomes light colored, or until all of the carbon is destroyed. If necessary, add a little HNO_3 and heat to the appearance of white SO_3 fumes. This treatment leaves the Sb in the proper condition for titration. Cool, add 50 cc. of water and 10 cc. of conc. HCl, and heat to solution of all that is soluble. Cool very thoroughly. Add 110 cc. more water and 10 cc. more acid. Cool again and then titrate at once with 0.1 N $KMnO_4$. The end-point is distinct but it fades after a short time. From the known Sb factor of the $KMnO_4$ solution, calculate the percentage of Sb.

NOTE.—The $KMnO_4$ solution should be standardized against C. P. antimony and the value of the solution in terms of Sb calculated, then the personal error in the end-point will be the same as in the actual analysis. The same $KMnO_4$ solution may be used as is described under Antimony in White Metals on page 193. The method of standardization is also there described.

Nickel.—Bronzes containing over 15% of Pb are likely also to contain nickel. For the determination, add 5 cc. of conc. H_2SO_4 to the solution from which Cu and Pb have been removed, and evaporate to SO_3 fumes. Dilute with 50 cc. of water and heat until all soluble salts are dissolved. Quickly pour this solution into 50 cc. of 30% NaOH solution. Heat to boiling, whereupon any Ni is precipitated as the apple green $Ni(OH)_2$. Dilute the solution to 150 cc., let the precipitate settle and filter through a weighed Gooch crucible. Wash thoroughly with hot water. Transfer the filtrate to the original beaker and dissolve all the $Ni(OH)_2$ through the Gooch crucible with the least possible amount of warm dil. H_2SO_4. Wash the Gooch crucible thoroughly and reprecipitate the Ni by pouring the solution into 10 cc. more of 30% NaOH solution diluted to about 30 cc. Heat to boiling. Let the precipitate settle and filter through the same Gooch crucible. Wash with hot water, ignite at a *white heat* and weigh as NiO. Calculate to Ni.

CALCULATION.—$NiO \times 0.7858 = Ni$.

NOTE.—If zinc is desired, and has not already been determined, add the second filtrate to the first, evaporate if necessary, and transfer to a 250-cc. beaker for electrolysis. Electrolyze as previously described under Zinc.

Aluminum.—This element is best determined after removal of zinc by electrolysis. Acidify the solution, which is now alkaline with NaOH, with conc. HCl and precipitate Fe and Al by adding a slight excess of NH_4OH and bringing to a boil. Let settle, filter and wash thoroughly with hot water. Ignite strongly in a platinum crucible and weigh as $Fe_2O_3+Al_2O_3$. Fuse with a considerable excess of anhydrous $KHSO_4$, take up the fusion with water and add sufficient conc. H_2SO_4 to give an acid concentration of about 5%. Warm the solution, pass through a Jones reductor and titrate the Fe with 0.05 N $KMnO_4$. Calculate to Fe_2O_3 and subtract from the weight of combined oxides to obtain the Al_2O_3. Calculate to Al.

CALCULATION.—$Al_2O_3 \times 0.5291 = Al$.

NOTE.—Inasmuch as the NaOH which has been used for the zinc electrolysis may contain an appreciable amount of Fe or Al, a blank determination should be made upon an equal amount of NaOH solution and any Fe and Al so obtained should be subtracted.

REFERENCE.—Price and Meade: "Technical Analysis of Brass and the Non-ferrous Alloys."

NICKEL SILVER

General.—Nickel Silver or German Silver is an alloy of Cu, Ni and Zn, containing occasionally small amounts of Pb, Fe, Mn and other minor impurities.

The method of analysis here described has been devised to take advantage of the well-known dimethylglyoxime precipitation of Ni and has given excellent satisfaction in this laboratory. Repeated comparisons with other methods have demonstrated that it gives accurate results and requires much less time and manipulation.

Copper.—Weigh 1 gram of the alloy into a beaker and dissolve in 15 cc. of dil. HNO_3 (1:1). When solution is complete and all nitrous fumes have been removed by boiling, dilute to a suitable volume for electrolysis, adding sufficient conc. HNO_3 to give an acid concentration of approximately 10%, if rotating electrodes are used, or 3% if the stationary type is employed. When using rotating electrodes and a 10% acid concentration, a current density increasing from 2 amperes at the beginning to 3 amperes near the end of the electrolysis, works very satisfactorily. In

the case of stationary electrodes and a 3% acid concentration, a current of 0.5 ampere is preferable. With rotating electrodes it is possible to remove all Cu in 1 hour. The metallic Cu is weighed as such on the electrode in the usual manner (see p. 182).

Lead.—Small amounts of Pb may be present as an impurity in the Zn used in the alloy. This will be entirely deposited on the anode as PbO_2 and may be weighed as such, calculating to metallic Pb.

CALCULATION.—$PbO_2 \times 0.8643 = Pb$.*

Nickel.—After the removal of the Cu and any Pb present transfer the solution to a 500-cc. volumetric flask and dilute to the mark. Pipette 100 cc., representing 0.2 gram, into a 600-cc. beaker. Make slightly but distinctly alkaline with NH_4OH, dilute to approximately 400 cc., heat to incipient boiling and filter off any $Fe(OH)_3$ precipitate. In the filtrate precipitate Ni as nickel glyoxime with 75 cc. of a saturated alcoholic solution of dimethylglyoxime. Heat at slightly below boiling for 1 hour, filter on a Gooch crucible, previously ignited and weighed, and wash with hot water.

Always test the first few cc. of the filtrate with a few drops of dimethylglyoxime reagent to make certain that no Ni remains unprecipitated. If it is found that some Ni still remains in the filtrate, return the latter to the beaker, add a few cc. more of the reagent, heat just below boiling for 15–20 minutes more and again filter. If all Ni is now precipitated, filter, wash, dry for 1 hour at 105–120° C., cool and weigh. Calculate to metallic Ni and multiply the result by 5 to correct for aliquoting.

CALCULATION.—Nickel glyoxime $\times 0.2032 = Ni$.

Zinc.—Transfer the filtrate from the Ni precipitate to a beaker and evaporate until the odor of NH_3 can no longer be detected. Cool the solution, transfer to a 500-cc. Erlenmeyer flask to avoid loss by spattering, add 5–6 cc. of conc. H_2SO_4 and evaporate the solution to the appearance of dense white fumes. Cool thoroughly and take up with water. Add 50 cc. of 30% NaOH solution and electrolyze on a copper-coated electrode according to the method on page 183. Weigh as metallic Zn and multiply the weight by 5 to correct for aliquoting.

* This is an empirical factor (see under Spelter, p. 174).

Impurities.—The determination of Pb has been already described. Fe, Mn and other impurities may be determined as in Brass and Bronze (see p. 184).

NOTE.—This method was adapted by H. C. Parish of this laboratory.

WHITE METALS

General.—The following procedures apply to the analysis of white alloys containing Sb, Sn, Cu, Zn, Pb, Fe, Ni, Mn, Al, and Mg. These are most conveniently divided into (1) Solders, (2) Babbitts, (3) Type Metals, and (4) Aluminum Alloys.

In those cases where two methods are given for the same determination, the first method is preferable and the alternative method should be used only for unusual samples or where specified for some special reason.

Sampling.—A representative sample is best obtained by the use of a hacksaw. The sawdust from the sample is especially desirable because the accuracy of some of the methods depends upon the fineness of the sample. In case a hacksaw cannot be used, obtain fine drillings with a small drill. Always pass a magnet through the sample before starting the analysis.

(1) SOLDER

General.—Solders usually consist of Sn and Pb with a small amount of Sb (and sometimes Cu and Zn) as impurity.

Tin (Volumetric Method).*—Weigh accurately 0.5 gram of the sample into a 300-cc. Erlenmeyer flask fitted with a 1-hole stopper carrying a 1-mm. capillary tube running into a 6-inch test-tube as shown in Fig. 9. Add to the flask 25 cc. of 10% Na_2CO_3 solution, 50 cc. of hot water, 50 cc. of conc. HCl and 1 drop of 5% $SbCl_3$ solution. Fill the test-tube one-third full with 10% Na_2CO_3 solution and insert the capillary tube into it. Place on the steam bath and heat until everything except any Cu and Sb is dissolved, which requires about 15 minutes. Remove the flask from the bath, fill the test-tube with 10% Na_2CO_3 solution and cool under running water. When cool add

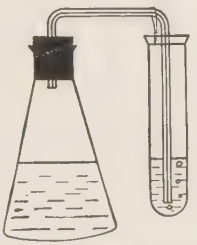


FIG. 9.—Apparatus for Determination of Tin in White Metals.

* If Pb is to be determined, use the gravimetric method for Sn.

to the flask 5 cc. of arrowroot starch solution, then 25 cc. of 10% Na_2CO_3 solution and titrate with 0.1 N iodine, covering the flask with a rubber washer which fits over the tip of the burette. The starch and Na_2CO_3 solution are best added from a pipette by inserting its tip between the stopper and the neck of the flask, allowing as little air as possible to enter the flask as it causes low results.

NOTE.—Standardize the iodine solution against 0.2500 gram of C. P. tin, following exactly the details of this method. Divide 0.2500 by the number of cc. of iodine solution used for titration. The quotient is the factor of the solution in terms of tin.

Tin (Gravimetric Method).—Weigh accurately 0.5 gram of the sample into a 250-cc. beaker, add 15 cc. of dil. HNO_3 (2 :1), cover immediately with a watch glass, and, when violent action ceases, boil until no more red fumes are evolved. Digest on the steam bath for 30 minutes. Dilute with 30 cc. of hot water. Let the precipitate settle, filter and wash with 2% HNO_3. Place the filter paper and contents in a weighed porcelain crucible. Smoke off the paper and ignite for 15 minutes in the full heat of a Tirrill burner. Cool in a desiccator and weigh the residue consisting of SnO_2 and Sb_2O_4, together with a small amount of PbO. Fuse the ignited precipitate with a mixture of finely powdered sulfur and Na_2CO_3, in the proportions of 1 part of precipitate to 3 parts each of S and Na_2CO_3, in a covered porcelain crucible until the odor of SO_2 has disappeared. Cool and dissolve the fusion in hot water; add an excess of Na_2SO_3 to convert any polysulfides to monosulfides; filter and wash the precipitate thoroughly.

This precipitate contains the Pb. Dissolve it in dil. HNO_3 (1 : 3) and determine the Pb electrolytically in the usual way, weighing as PbO_2 on the anode. Calculate the weight thus found to PbO and subtract from the original weight of the precipitate. (Also calculate it to Pb and add to the main Pb determination as later described.) Also calculate the Sb (determined as described later) to Sb_2O_4 and subtract this from the original precipitate. The remainder is SnO_2. Calculate this to Sn.

CALCULATIONS.—$Sb \times 1.2628 = Sb_2O_4$.

$PbO_2 \times 0.9331 = PbO$.

$PbO_2 \times 0.8643 = Pb$.*

$SnO_2 \times 0.7877 = Sn$.

* Empirical factor.

Antimony.—Weigh accurately 1 gram of the sample into a 500-cc. Pyrex Erlenmeyer flask. Add 15 cc. of conc. H_2SO_4 and 4–5 grams of K_2SO_4. Heat until the residue is perfectly white, but do not drive off all the free H_2SO_4, which makes the melt hard on cooling. Cool thoroughly and add 50 cc. of 10% tartaric acid solution and 10 cc. of conc. HCl. Heat until all soluble matter is dissolved, cool very thoroughly, add 110 cc. of water and 10 cc. more of conc. HCl, cool again and titrate at once with 0.1 N $KMnO_4$. The end-point is distinct but fades quite rapidly. From the known strength of the $KMnO_4$ solution calculate the percentage of Sb.

STANDARDIZATION.—Standardize the $KMnO_4$ solution against C. P. antimony and calculate the value of the solution in terms of Sb; then the personal error in the end-point will be the same as in the actual analysis. Use the following procedure:

Weigh out exactly 0.1500 gram of C. P. antimony and an equal quantity of C. P. tin. Place in a 500-cc. Erlenmeyer flask, add 15 cc. of conc. H_2SO_4 and 4–5 grams of K_2SO_4. Heat until the metals are in solution or entirely decomposed and all separated S is driven off. Do not drive off enough SO_3 to cause the melt to harden on cooling. Cool, add 50 cc. of 10% tartaric acid solution and 10 cc. of conc. HCl, and heat until a clear solution is obtained. Cool the solution to tap-water temperature, then add 110 cc. more of water and 10 cc. more of conc. HCl. Cool again and titrate at once to a pink color with the $KMnO_4$ solution.

CALCULATION.—$\text{Sb factor} = \dfrac{0.1500}{\text{cc. of } KMnO_4 \text{ used}}$.

Lead.—To the filtrate from the *gravimetric* Sn determination add 10 cc. of conc. H_2SO_4, and evaporate until copious fumes of SO_3 are evolved. Cool thoroughly and take up with 100 cc. of water; boil and let stand until perfectly cold (preferably overnight). Filter the $PbSO_4$ on a weighed, ignited Gooch crucible and wash with 5% H_2SO_4, and then with 50% ethyl alcohol, or No. 30 specially denatured, until the washings are free from acid. Do not run alcohol into the main filtrate as it will interfere with subsequent electrolysis for Cu. It is used merely for removing the acid from the $PbSO_4$. Place the Gooch crucible inside of a platinum crucible and ignite. Cool in a desiccator and weigh as $PbSO_4$. Calculate to Pb.

CALCULATION.—$PbSO_4 \times 0.6833 = Pb$.

NOTE.—Any Pb found in purifying the tin-antimony oxides, as previously described, must be added to the amount here found.

Copper.—Dilute the filtrate from the Pb determination to approximately 200 cc. and electrolyze for copper in a 250-cc. beaker, as described under Brass and Bronze (p. 182).

Zinc.—To the solution from which Cu has been removed, add 75 cc. of 30% NaOH solution and electrolyze as described under Brass and Bronze (p. 183).

(2) HIGH-TIN BABBITT METALS

Tin.—Weigh accurately 0.5 gram of the sample into a 250-cc. beaker and determine Sn and Sb as oxides, as described above under Solder (Gravimetric Method).

Antimony.—Using a 1-gram sample, determine the Sb by the method previously described for Sb in Solder.

Copper and Lead.—*Method I.**—Treat 1 gram of the finely divided sample in a 250-cc. covered beaker with 10 cc. of aqua regia (1 part conc. HNO_3, 3 parts conc. HCl). Add a little $KClO_3$ and heat. Then add a little tartaric acid, dilute with water and make slightly alkaline with NaOH. If a precipitate forms, make acid again with HCl, add more tartaric acid and make alkaline with NaOH. When a clear solution is obtained, add 25 cc. of a saturated Na_2S solution and digest on the steam bath for 30 minutes, stirring frequently. Let the precipitate settle, filter on an asbestos mat in a loose-bottomed Gooch crucible and wash with 2% Na_2S solution. Transfer the asbestos mat and precipitate to a small beaker, dissolve the sulfides in 20 cc. of conc. HNO_3, dilute to about 100 cc., filter, dilute the filtrate to 200 cc. and determine the Cu and Pb by simultaneous electrolysis.

Method II.—Dilute the filtrate from the Sn determination to about 200 cc. and add conc. HNO_3 until the solution contains approximately 10%. Electrolyze as described under Copper in Brass and Bronze (p. 182). The Pb will be deposited at the same time on the anode as PbO_2. Calculate its weight to metallic Pb.

* If Sn has been determined, use Method II.

CALCULATION.—$PbO_2 \times 0.8643 = Pb$.*

NOTE.—To the Cu and Pb thus determined must be added the Cu and Pb recovered as impurities from the SnO_2 by the procedure previously described in the method for Solder. At the same time that the Pb from the purification of the SnO_2 is deposited on the anode, the Cu is deposited on the cathode.

Zinc.—To the liquid from which the Cu and Pb have been removed add 2–3 cc. of conc. H_2SO_4, and evaporate to copious white fumes of SO_3. Cool, add 50 cc. of 30% NaOH solution, and electrolyze for Zn as described under Brass and Bronze (p. 183).

(3) HIGH-LEAD BABBITT METALS AND TYPE METALS (INCLUDING LINOTYPE, STEREOTYPE, MONOTYPE, ETC.)

Tin (Volumetric Method).—Heat 1 gram of the sample, accurately weighed, in a 300-cc. Erlenmeyer flask, with 50 cc. of conc. HCl on the steam bath until all action ceases. While the solution is still hot add 2 or 3 small crystals of $KClO_3$ at a time and shake until a clear solution is obtained. Avoid an excess of $KClO_3$. Add 50 cc. of conc. HCl, 100 cc. of hot water, 2 grams of steel drillings (see note 1) and 25 cc. of 10% Na_2CO_3 solution, in the order given. Quickly insert the stopper carrying the bent capillary tube and test-tube, as shown on page 191. The test-tube must be one-third full of 10% Na_2CO_3 solution. Place on the steam bath and heat until the steel is entirely dissolved (see note 2). Fill the test-tube with 10% Na_2CO_3 solution and cool the flask to tap water temperature. Add to the flask 5 cc. of arrowroot starch, then 25 cc. of 10% Na_2CO_3 solution, each from a pipette, and complete the determination as described in the volumetric method for Tin in Solder (p. 191), being careful to exclude air as completely as possible.

NOTES.—(1) Plain carbon steel drillings, containing 0.35–0.60% carbon, give the best results. They must not be too fine.

(2) All yellow color due to chlorine should be destroyed. If not, the analysis must be repeated, as too much $KClO_3$ has been added and the results will be low.

(3) Some trouble may be experienced at first in seeing the end-point on account of suspended carbon. This can best be seen by looking down through the bottom of the flask where light shows through the solution. As soon as the blue end-point is reached, the solution becomes opaque at

* Empirical factor.

this point; and as soon as the carbon settles, the deep blue color can be seen distinctly.

(4) Always run a blank determination, using 0.1500 gram of pure Sb (but no Sn) and proceeding exactly as described above. Subtract this blank titration from the total titration.

(5) Standardize the iodine solution used against pure Sn exactly as described under the determination of Sn in Solder (p. 192).

Tin (Gravimetric Method).—Weigh accurately 1 gram of the sample into a 250-cc. beaker, together with sufficient C. P. tin so that the ratio Sn:Sb is at least 3:1. Determine the Sn gravimetrically as above described under Solder (p. 192), carrying through the purification of the oxides as there described.

NOTE.—The amount of Sn added should be calculated to SnO_2 and, together with the impurities and Sb_2O_4, deducted from the total weight of the precipitate.

CALCULATION.—$Sn \times 1.2696 = SnO_2$.

Antimony.—Determine Sb on 0.5 gram of the sample exactly as described under Solder (p. 193).

Lead.—Treat 0.5 gram of the finely divided sample in a 250-cc. Erlenmeyer flask with 4–7 grams of tartaric acid (depending upon the amount of Sn and Sb present), 15 cc. of water and 4 cc. of conc. HNO_3, and heat on the steam bath until a clear solution is obtained. Add cautiously and with constant stirring 4 cc. of conc. H_2SO_4, dilute with 50 cc. of water and let cool until the precipitate settles completely (at least 1 hour). All Pb will be precipitated as $PbSO_4$. Filter on a Gooch crucible, wash with 5% H_2SO_4 and then with 50% alcohol until the washings are free from acid. Set the crucible inside a platinum crucible, ignite, cool and weigh as $PbSO_4$, as described under Lead in Solder (p. 193).

Copper.—If Cu is desired, electrolyze the solution as previously described for Cu in Solder, after removing Sn and Sb* by the gravimetric method for Sn and removing Pb by evaporation to SO_3 fumes after the addition of 5 cc. of conc. H_2SO_4.

Zinc.—If a Zn determination is desired, add 75 cc. of 30% NaOH solution to the liquid after the electrolysis for Cu and electrolyze as previously described under Zinc in Solder.

*Add sufficient pure Sn to bring the ratio Sn : Sb to at least 3:1, otherwise not all the Sb will be removed.

(4) Aluminum Alloys

General.—In accordance with common practice in analysis of alloys high in Al, the percentages of all other elements present are determined and the Al taken by difference. This is on account of the difficulties that are usually encountered in determining Al where it is present in such large amounts. Make all the determinations in duplicate. It is also always advisable to make a qualitative analysis before attempting quantitative work.

Silicon.—Dissolve 1 gram, accurately weighed, of well-mixed drillings in 35 cc. of acid mixture (see below), using a porcelain dish covered with a watch glass. When the drillings are completely dissolved, evaporate the solution to dryness and bake on the hot plate for at least 0.5 hour to insure complete dehydration of the SiO_2. Take up the residue with dil. HCl (1:4), filter, and wash with hot water. Ignite and weigh in a platinum crucible. Evaporate with about 10 cc. of HF and a drop of H_2SO_4 and again ignite and weigh. The loss is SiO_2. Calculate to Si.

Calculation.—$SiO_2 \times 0.4672 = Si$.

Acid Mixture.—Pour 150 cc. of conc. H_2SO_4 into 450 cc. of water. Cool and add 100 cc. of conc. HNO_3 and then 300 cc. of conc. HCl.

Aluminum.—If for any reason it is desired to make a direct determination of Al, dilute the filtrate from the Si determination to 500 cc. in a volumetric flask, and, after thoroughly mixing, take a 100-cc. aliquot for analysis. Dilute to approximately 300 cc., add a pinch of tannic acid and a slight excess of NH_4OH. Boil until the odor of NH_3 is nearly gone, filter and wash with hot water. Dissolve the precipitate in hot dil. HCl (1:1), add a pinch of tannic acid, reprecipitate exactly as previously, and wash with hot water. Dry the paper and residue in the funnel, transfer to a platinum crucible, burn off the paper and finally ignite with a blast lamp in a platinum crucible to constant weight and weigh as $Al_2O_3 + Fe_2O_3$. Subtract the Fe_2O_3 present (as later determined) and calculate the remainder to Al.

Calculation.—$Al_2O_3 \times 0.5291 = Al$.

Manganese.—Dissolve 1 gram of the finely divided sample in 50 cc. of dil. HNO_3 (1:3) in a 200-cc. Erlenmeyer flask. Since Al dissolves very slowly in HNO_3, this may require some time.

When entirely in solution, cool to about 15° C., add 0.5 gram of sodium bismuthate and agitate for a few minutes. Add 50 cc. of 3% HNO_3, and filter through an extra-porous alundum thimble. Wash with 50–100 cc. of the same acid and finally with water. Do not let the solution come in contact with rubber connections. Titrate the filtrate in the flask with standard sodium arsenite solution (see note 1) as described under Manganese in Steel (p. 137).

NOTES.—(1) The total amount of Mn titrated in this way should not be over 0.0125 gram. If, therefore, the material contains over 1.25% of Mn, use a 0.5-gram sample, or less.

(2) *Arsenite Solution.*—Use the same arsenite solution as for titrating Mn in Steel (see p. 137).

(3) In case the sample is not fine, it may be necessary to use a small amount of HCl to effect solution, and subsequently drive this off by evaporating to a small volume with successive portions of conc. HNO_3, before proceeding with the method above described.

Tin.—Weigh accurately a 1-gram sample, together with approximately 5 grams of NaOH,* into a beaker and add just enough water to cover the sample. When violent action has ceased, dilute to about 100 cc. and boil for 4–5 minutes. Cool, filter, and wash the residue with hot water until *free from alkali*. The Al and practically all the Zn are dissolved, while other metals remain unaffected. Save the filtrate for subsequent determination of Zn.

Wash the bulk of the residue from the NaOH treatment into a beaker. Ash the filter and add it to the beaker. Add 20 cc. of conc. HNO_3, evaporate to approximately 10 cc. and dilute to 50 cc. with hot water. Filter, wash, ignite in a weighed porcelain crucible, and weigh as SnO_2. Calculate to Sn.

CALCULATION.—$SnO_2 \times 0.7877 = Sn$.

Copper and Lead.—Bring the volume of the filtrate to 200 cc. and add 10 cc. of conc. HNO_3. Electrolyze for Cu and Pb as described under Brass and Bronze (p. 182).

Iron.—Make the solution from the Cu and Pb determination alkaline with NH_4OH, and boil. Filter off the precipitate of $Fe(OH)_3$, wash with hot water and dissolve from the filter by pouring hot dil. H_2SO_4 upon it, catching the solution in a beaker.

* If iron is to be determined, the NaOH must be weighed and a correction applied for the amount of Fe which it contains.

Dilute this solution until the H_2SO_4 present is approximately 5%. Heat nearly to boiling and pass through a Jones reductor. Cool and titrate with 0.1 N $KMnO_4$ solution.

CALCULATION.—1 cc. 0.1 N $KMnO_4$ = 0.005584 gram Fe.
= 0.007984 gram Fe_2O_3.

NOTE.—Run a blank on the reductor, using the same amount and volume of acid, and subtract the blank from the titration of the sample (see p. 186).

Nickel.—Heat to boiling the above filtrate from the $Fe(OH)_3$ precipitate and add a 1% solution of dimethylglyoxime in alcohol, until the amount of reagent is about 5 times that of the Ni believed to be present. A large excess does no harm but it is unnecessary and the reagent is very expensive. Let the solution stand on the water bath for 30 minutes and filter while still hot through a weighed porcelain Gooch crucible. Wash with hot water and dry to constant weight at 110–120° C. Weigh as nickel glyoxime, $C_8H_{14}N_4O_4Ni$, and calculate to Ni.

CALCULATION.—$C_8H_{14}N_4O_4Ni \times 0.2032 = Ni$.

Zinc.—Dilute the filtrate from the original NaOH treatment in the tin determination to 200 cc. and determine the Zn by electrolysis as described in the method for Brass and Bronze (p. 183). Discard the solution after the Zn is removed. Some Zn may remain insoluble in NaOH and should be recovered as follows: Boil the filtrate from the Ni determination until the free NH_3 is expelled. Acidify with dil. H_2SO_4, adding the equivalent of 2–3 cc. of conc. H_2SO_4 in excess. Transfer to a 500-cc. Pyrex Erlenmeyer flask and evaporate to white SO_3 fumes. If the solution is dark colored, add a few cc. of conc. HNO_3 and again evaporate to SO_3 fumes. Take up with water, cool, add 50 cc. of 30% NaOH solution, dilute to 200 cc. in a 250-cc. beaker and electrolyze for Zn as previously described. Add the Zn obtained here to that obtained by electrolysis of the filtrate from the original NaOH treatment.

Magnesium.—After any Zn present has been removed by electrolysis, acidify with conc. HCl, adding about 10 cc. in excess. Dilute to about 300 cc., cool to tap-water temperature and add 30 cc. of a saturated solution of microcosmic salt, $NH_4NaHPO_4 \cdot 4H_2O$. Add NH_4OH drop by drop, stirring vigorously to make the precipitate crystalline. Then add an excess of conc. NH_4OH,

approximately 10% of the volume of the whole solution. Let stand overnight, filter through a weighed Gooch crucible, and wash with cold water containing 5% of conc. NH_4OH and 5% of NH_4NO_3. Ignite until completely white. Weigh as $Mg_2P_2O_7$ and calculate to Mg.

CALCULATION.—$Mg_2P_2O_7 \times 0.2184 = Mg$.

REFERENCES.—Price and Meade: "Technical Analysis of Brass and Non-ferrous Alloys;" E. Blough: "Analysis of Aluminum and Its Commercial Alloys."

MERCURY IN ZINC AMALGAM

General.—So-called Battery Zincs are often made of zinc amalgam containing 1–3% of mercury. The following method is a convenient one for the determination of the amount of Hg and gives accurate results.

Determination.—Dissolve 4–5 grams of the finely divided alloy in about 75 cc. of dil. HCl (1:1) and boil for 2–3 hours. This dissolves Zn, whereas any Hg and Pb present will be separated as metal.

Decant off the solution, wash the residue several times with hot water and transfer to a porcelain crucible. Dry at 100° C., cool in a desiccator and weigh. Then ignite at a red heat and again cool in a desiccator and weigh. The loss, represented by the difference in weight, is Hg.

NOTE.—The ignition should be conducted under a hood and care taken not to breathe the mercury fumes, which are poisonous.

REFERENCE.—This method has been used for some time at the laboratory of the N. Y., N. H. & H. Railroad.

TESTING OF GALVANIZING OR SHERADIZING ON IRON AND STEEL

General.—There are two methods of applying a protective zinc coating to iron and steel.

Galvanizing deposits a layer of metallic Zn on the surface and gives a bright, smooth, shiny surface generally showing the characteristic crystalline structure of Zn.

Sheradizing forms a dull gray (nearly slate-colored) coating generally more or less rough. This coating is not metallic Zn as in the case of galvanizing but is a mixture of metallic Zn and a Zn-Fe alloy.

The Preece test, described herewith, was originally designed for galvanized articles and particular care must be employed, in applying it to sheradized articles, to brush the specimen vigorously with a wire brush after each dip and not to be deceived by an apparent plating of copper which can be removed by further dips and scrubbing.

Cleaning.—Clean the samples before testing, first with CCl_4, benzine or turpentine, and cotton waste (not with a brush),* and then thoroughly rinse in clean water and wipe dry with clean cotton waste. The samples must be clean and dry before each immersion in the test solution.

Test Solution.—Dissolve commercial copper sulfate crystals in cold water, in the proportion of about 36 parts by weight of crystals to 100 parts of water. Neutralize the solution by the addition of an excess of chemically pure CuO. The presence of an excess of CuO will be shown by the sediment of this reagent at the bottom of the containing vessel.

Filter the neutralized solution before use, by passing through filter paper. The filtered solution must have a sp. gr. of 1.186 at 65° F.† (reading the scale at the level of the solution) at the beginning of each test. In case the filtered solution is high in sp. gr., add clean water to reduce the sp. gr. to 1.186 at 65° F. In case the filtered solution is low in sp. gr., add a filtered solution of a higher sp. gr.

As soon as the stronger solution is taken from the vessel containing the unfiltered neutralized stock solution, additional crystals and water must be added to the stock solution. An excess of CuO must always be kept in the unfiltered stock solution.

Quantity of Solution.—Test wire samples in a glass jar of at least 2 inches inside diameter. Fill the jar without the wire samples with standard solution to a depth of at least 4 inches. Test hardware samples in a glass or earthenware jar containing at least 0.5 pint of standard solution for each hardware sample. Solutions must not be used for more than 1 series of 4 immersions.

Samples.—Not more than 7 wires are to be simultaneously immersed, and not more than 1 sample of galvanized material

* Except for sheradized articles.

† This is equivalent to a reading of 22.7° on a Baumé hydrometer at 65° F

other than wire, in the specific quantity of solution. Do not group the samples or twist them together, but keep them well separated so as to permit the action of the solution to be uniform upon all immersed portions.

Test.—Immerse the clean and dry samples in the required quantity of standard solution in accordance with the following cycle of immersions. The temperature of the solution must be maintained between 62–68° F. at all times during the test.

First.—Immerse for 1 minute, wash and wipe dry.*

Second.—Immerse for 1 minute, wash and wipe dry.

Third.—Immerse for 1 minute, wash and wipe dry.

Fourth.—Immerse for 1 minute, wash and wipe dry.

After each immersion immediately wash the samples in clean water at a temperature between 62–68° F., and wipe dry with cotton waste.*

In testing wire of No. 13 B. W. G. and smaller sizes, reduce the time of the fourth dip to 0.5 minute.

Interpretation.—If the samples as tested above show bright, firmly adhering metallic copper deposits, they are considered as having failed to pass the test.

In the case of sheradized articles there will be a copper deposit formed on each dip, due to the Fe-Zn alloy. This deposit, however, is not firmly adhering nor of the typical bright color of the Cu plate which indicates failure. It can be removed by vigorous scrubbing with a wire brush under running water and care must be taken not to reject sheradized articles unless they show a firmly adhering Cu deposit which is bright colored and cannot be removed by wire-brushing or by further dipping and brushing.

Cu deposits on Zn or within 1 inch of the cut end may be disregarded.

If 1 wire in a group of 7 wires immersed together shows a Cu deposit, or if there is reasonable doubt as to the presence of the Cu deposit, 2 check tests should be made upon the 7 wires and the report based on the majority of the sets of tests.

In case the article has a cut screw, the thread shall stand one 1-minute immersion; the rest of the article shall withstand the

* In the case of sheradized materials the specimens must be quickly removed to running water after each dip and brushed vigorously with a wire brush while in the running water.

specified 4 immersions. The threads of nuts are not required to stand the galvanizing test.

Reference.—Amer. Telephone & Telegraph Co. Specification 3110, Feb. 3, 1908.

TINNING TEST FOR TINNED IRON AND STEEL

Method of American Electric Railway Engineering Association. *Preparation of Samples.*—Samples of the wire or other material to be tested must be thoroughly cleaned with alcohol.

Tinning Test.—Immerse in HCl (sp. gr. 1.088 at 15.5° C.) for exactly 1 minute. Rinse in pure water and immerse in an aqueous solution of sodium sulfide (sp. gr. 1.142, or 28° Baumé) for exactly 30 seconds. Again wash in pure water and repeat the operation 3 times. At the end of the fourth immersion in Na_2S, the wire should show no sign of blackening.

Sodium Sulfide Solution.—The Na_2S solution must contain an excess of sulfur and have sufficient strength to thoroughly blacken a piece of untinned Cu wire in 5 seconds. Each new solution made up must be tested for strength with a piece of untinned Cu wire.

Method of American Telephone and Telegraph Co.—Immerse the samples of wire or other material to be tested in a current of pure H_2S gas, saturated with water vapor, at a temperature of not less than 24° C. nor more than 26° C., for 4 hours. At the end of this time the samples should show no signs of blackening.

NICKEL PLATING SOLUTION

General.—This method is designed for the analysis of nickel plating solutions consisting of a soluble Ni salt, boric acid and ammonium chloride dissolved in water in the proportions of approximately 3 ounces of metallic Ni, 2 ounces of H_3BO_3 and 1.5 ounces of NH_4Cl per gallon. Results are usually reported in avoirdupois ounces per gallon.

Nickel.—The Ni may be determined either by electrolysis or by titration with standard KCN solution. The titration method is much quicker.

(*a*) *By Titration.*—With an accurate pipette measure 2 cc. of the solution into a 400-cc. beaker. Add 10 cc. of dil. HNO_3 (1 : 1) and boil until red fumes have been driven off; then add 100 cc.

of citric acid solution and proceed as under the determination of Nickel in Alloy Steel (p. 150). Calculate the weight of Ni (in grams) in 2 cc. of the solution and multiply the result by 66.8 to obtain ounces per gallon.

(*b*) *By Electrolysis.*—Pipette 5 cc. of the solution into a 250-cc. beaker, add 5 cc. of conc. H_2SO_4 and evaporate to strong white fumes on a hot plate. Cool and dilute with cold water to about 100 cc. Neutralize carefully with NH_4OH and add 30 cc. of conc. NH_4OH in excess. Electrolize with a rotating cathode until all the Ni has been removed. Weigh as metallic Ni and calculate to ounces per gallon.

CALCULATION.—Grams Ni in 5 cc. $\times 26.70$ = ounces per gallon.

Ammonium Chloride.—Dilute 5 cc. of the solution, accurately measured, in a beaker with about 200 cc. of water. Precipitate slowly with an excess of $AgNO_3$ solution and stir briskly. Set aside in a dark place until the AgCl is completely settled. Filter on a weighed Gooch crucible, wash with cold water, set the crucible inside of a larger platinum crucible and ignite until the edges of the precipitate just *begin* to fuse. Cool in a desiccator and weigh as AgCl. Calculate to ounces of NH_4Cl per gallon.

CALCULATION.—Grams of AgCl $\times 9.965$ = ounces NH_4Cl per gallon.

Boric Acid.—Pipette 5 cc. of the solution into a beaker and dilute to 200 cc. with water. Add 50 cc. of 0.5 N NaOH solution. Stir thoroughly and filter out the precipitate of $Ni(OH)_2$ on a Büchner funnel fitted with a close-fitting filter paper, using suction. Wash thoroughly with water. To the filtrate add a few drops of methyl orange indicator and exactly neutralize with 0.5 N HCl. Then add about 1 cc. of phenolphthalein indicator and 5 grams of mannite and titrate the H_3BO_3 with 0.1 N NaOH to the first appearance of a permanent pink color. Add 2 or 3 grams more of mannite and if the pink color is discharged, continue the addition of 0.1 N NaOH until a permanent pink color is finally reached. Calculate the titration to H_3BO_3.

CALCULATION.—1 cc. 0.1 N NaOH = 0.006184 gram H_3BO_3.

Grams of H_3BO_3 in 5 cc. $\times 26.70$ = ounces per gallon.

SILVER PLATING SOLUTION

General.—This method is designed for the analysis of silver plating solutions containing approximately 2 ounces of Ag per

gallon, the Ag being in solution in excess of NaCN. Results of the analysis are usually expressed in Troy ounces per gallon.

Silver.—Pipette 5 cc. of the solution into a beaker, add 25 cc. of water and 15 cc. of conc. HNO_3. Boil on a hot plate under a hood with a good draft to remove the HCN. Dilute with water to about 200 cc. and add slowly an excess of NaCl solution. Stir briskly and set aside in a dark place until the AgCl has settled clear. Filter on a weighed Gooch crucible, wash well with cold water, set the crucible inside of a larger platinum crucible and heat until the edges of the precipitate just *begin* to fuse. Cool in a desiccator and weigh. Calculate to metallic Ag.

CALCULATION.—Grams of AgCl $\times 18.32$ = Troy ounces of Ag per gallon.

NOTE.—If it is desired to express results in avoirdupois ounces per gallon, use the factor 20.09.

Free Sodium Cyanide.—Pipette 5 cc. of the solution into a beaker, add about 100 cc. of water and titrate with 0.1 N $AgNO_3$ solution, drop by drop, stirring constantly, to the first appearance of a permanent turbidity. Calculate the titration to NaCN.

CALCULATION.—1 cc. 0.1 N $AgNO_3$ = 0.009801 gram NaCN.

Grams NaCN in 5 cc. $\times 24.34$ = Troy ounces per gallon.

NOTE.—If it is desired to express results in avoirdupois ounces per gallon, use the factor 26.70.

Total Sodium Cyanide.—The Ag is in solution in the form of a double cyanide, AgCN·NaCN. Calculate (in terms of NaCN) the amount of CN combined with the Ag previously determined. This gives the combined NaCN, which added to the free NaCN previously obtained gives total NaCN.

CALCULATION.—Combined NaCN = Ag $\times 0.9085$.

Sodium Carbonate.—Old plating solutions which have been used in the tanks for some time contain more or less Na_2CO_3 formed by decomposition of the cyanide. The amount may be determined as follows:

To about 150 cc. of alcohol contained in a beaker add a few drops of phenolphthalein solution and then sufficient 0.1 N NaOH to produce a slight pink color. Into this solution pipette 5 cc.

of the sample. Filter out the insoluble Na_2CO_3 and wash with neutralized alcohol. Some of the residue usually sticks to the beaker. It is not necessary to remove this, simply rinse the beaker with neutralized alcohol and pour this on the filter. Place the filter paper containing the precipitate in the original beaker, dissolve in water and titrate the solution, with the filter paper in it, with 0.1 N HCl and methyl orange. Calculate the titration to Na_2CO_3.

CALCULATION.—1 cc. 0.1 N HCl = 0.0053 gram Na_2CO_3.

Grams Na_2CO_3 in 5 cc. $\times$ 24.34 = Troy ounces per gallon.

CHAPTER V

ANALYSIS OF FUELS

COAL SAMPLING

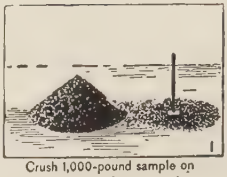
General.—The main object in taking a sample of coal is to secure a small portion of the coal which represents as nearly as possible the entire shipment. It is extremely important that the sample be properly taken, as in many cases it is entirely impossible to obtain another sample. Wherever possible collect the sample while the coal is being loaded into or unloaded from cars, boats, trucks or other conveyor. When coal is being crushed as received, it is often advantageous to take the sample as it comes from the crusher. Samples taken only from the surface of piles or bins are generally unreliable.

Gross Sample.—In collecting the sample use a shovel or other tool which will take equal portions. For slack coal or small sizes of anthracite each shovelful may be as small as 5–10 pounds, but for lump coal or run-of-mine the amount of each shovelful should be 10–30 pounds. The total sample obtained in this way is called the gross sample. Wherever possible the gross sample should not be less than 1000 pounds, except in the case of slack coal and small sizes of anthracite (not greater than $\frac{3}{4}$ inch), where 500 pounds are sufficient. If the coal contains an unusual amount of slate or other impurities and if the pieces of such impurities are very large, collect a gross sample of 1500 pounds or more. The gross sample should contain the same proportions of lump, fine, and impurities as in the coal sampled. The gross sample should preferably be collected in a large receptacle with cover attached.

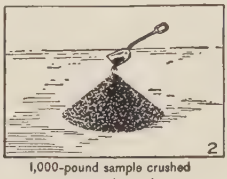
A gross sample should be taken for each 1000 tons or less delivered, unless otherwise specified.

When necessary to sample from loaded car or in bins or piles, the shovelfuls should be taken by a systematic plan in sufficient number to make the proper gross sample and from as nearly all

First stage in the preparation of 1,000-pound sample



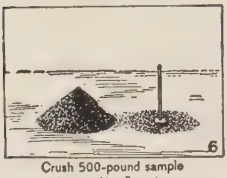
Crush 1,000-pound sample on hard, clean surface to 1″ size



1,000-pound sample crushed to 1″ and coned

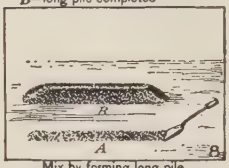
Mix by forming long pile.
A—spreading out first shovelful.
B—long pile completed

Second stage.



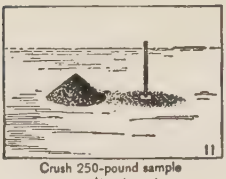
Crush 500-pound sample (fig. 5, *A*) to ¾″ size

500 pounds crushed to ¾″ and coned

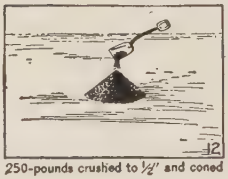


Mix by forming long pile.
A—spreading out first shovelful.
B—long pile completed

Third stage.



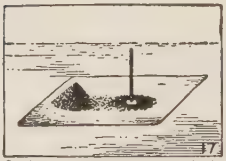
Crush 250-pound sample (fig. 10, *A*) to ½″ size



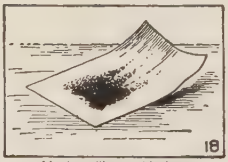
250-pounds crushed to ½″ and coned

Mix by forming new cone

Fourth stage.



Crush 125-pound sample (fig. 16: *A*, *A*) on blanket to ⅜″ size



Mix by rolling on blanket

Form cone after mixing

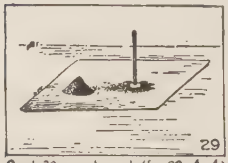
Fifth stage

Crush 60-pound sample (fig. 22: *A*, *A*) to ¼″ size

Mix by rolling on blanket

Form cone after mixing

Sixth stage.



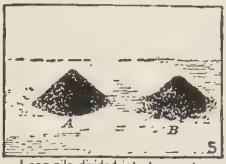
Crush 30-pound sample (fig. 28: *A*, *A*) to 3/16″ or 4-mesh size

Mix by rolling on blanket

Form cone after mixing

FIG. 10.—Method of Preparing a

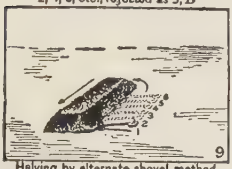
Halving by alternate shovel method. Shovelfuls 1, 3, 5, etc., reserved as 5, *A*; 2, 4, 6, etc., rejected as 5, *B*



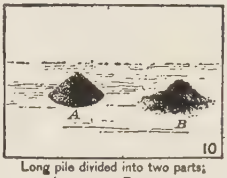
Long pile divided into two parts; *A*—reserve; *B*—reject

NOTE

SELECT A HARD, CLEAN SURFACE, FREE OF CRACKS AND PROTECTED FROM RAIN, SNOW, WIND, AND BEATING SUN. DO NOT LET CINDERS, SAND, CHIPPINGS FROM FLOOR, OR ANY OTHER FOREIGN MATTER GET INTO THE SAMPLE. PROTECT SAMPLE FROM LOSS OR GAIN IN MOISTURE



Halving by alternate shovel method. Shovelfuls 1, 3, 5, etc., reserved as 10, *A*; 2, 4, 6, etc., rejected as 10, *B*

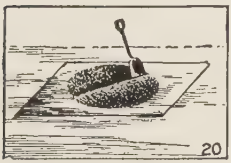


Long pile divided into two parts; *A*—reserve; *B*—reject

Quarter after flattening cone

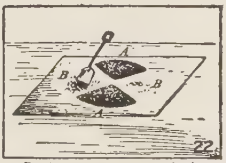
Sample divided into quarters

Retain opposite quarters *A*, *A*. Reject quarters *B*, *B*



Quarter after flattening cone

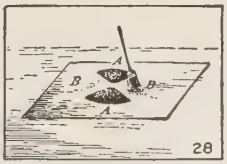
Sample divided into quarters



Retain opposite quarters *A*, *A*. Reject quarters *B*, *B*

Quarter after flattening cone

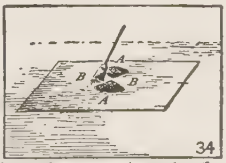
Sample divided into quarters



Retain opposite quarters *A*, *A*. Reject quarters *B*, *B*

Quarter after flattening cone

Sample divided into quarters



Fill two 5-pound sample containers from *A*, *A*, one for laboratory, one for reserve

Sample of Coal by Hand.

parts of the pile as possible, discarding the outer surface and securing as nearly as possible the same amount from the top, middle and bottom of the coal.

Laboratory Sample.—Having secured the gross sample (protected from the weather to avoid loss or gain in moisture), reduce it down to a smaller sample as follows (see Fig. 10):

Break down large lumps of coal and impurities on a clean, hard, dry floor with a suitable maul or sledge until, as judged by the eye, there are no pieces larger than specified (see Table VII). Then thoroughly mix by shoveling over and over and form in a conical pile. Reduce this down by the alternate shovel method as follows: Take a shovelful from the conical pile and spread it out in a straight line having a width equal to the width of the shovel and a length of 5–10 feet. Then spread the next shovelful in the opposite direction over the top of the first. Continue this, occasionally flattening the pile, until all the coal has been formed into one long narrow pile. Starting at one end, on the side, take one shovelful from the bottom and set it aside. Then advance along the side of the pile a distance equal to the width of the shovel, take a second shovelful and set it aside in a second pile. Again advance in the same direction one shovel-width, take a third shovelful and add to the first. Take the fourth shovelful in the same manner and add it to the second. Proceed in this way, putting even shovelfuls in one pile and odd in another. Continue to advance in the same direction around the original pile, so that its size will be gradually reduced in a uniform manner. Finally there will be two piles containing approximately the same amount of coal. Discard one of these. Spread out the other and crush down to the size indicated in the table. Then form in a conical pile, followed by a long narrow pile, and again reduce by the alternate shovel method.

After the gross sample has been reduced by the above method to approximately 250 pounds, further reduce it in quantity by the quartering method. Before each quartering crush the sample to the prescribed fineness. For quartering, form into a conical pile, and flatten out the cone. Divide with a shovel or board into 4 equal segments and discard 2 opposite quarters. Mix the 2 remaining quarters, crush down to proper size, mix, reform into a conical pile and quarter as before. Continue the process until

no lumps are greater than $\frac{3}{16}$ inch (or 4-mesh screen size) and the final sample amounts to about 1–2 quarts.

TABLE VII—REQUIRED FINENESS FOR GIVEN WEIGHT OF COAL SAMPLE

Weight of sample	Largest size allowable
1,000 pounds or over	1 inch
500 pounds	$\frac{3}{4}$ inch
250 pounds	$\frac{1}{2}$ inch
125 pounds	$\frac{3}{8}$ inch
60 pounds	$\frac{1}{4}$ inch
30 pounds or less	$\frac{3}{16}$ inch (4-mesh)

In reducing the gross sample, when the quantity reaches less than 125 pounds it should be placed on a mixing canvas about 6 × 8 feet and mixed by raising first one end of the canvas and then the other, so as to roll the coal back and forth.

The sample should be worked down as rapidly as possible to avoid loss of moisture and immediately placed in an air tight can or container. The outside of the container should be plainly marked and the corresponding description placed inside.

Data.—The following data should accompany the sample:

Coal delivered to.....
Sampled by.....Date.....
Amount taken for original sample.....
Amount of coal sample represents.....
Sampled from barge, car or pile.....
Car (initial and number).....
Barge or vessel.....
Trade name of coal.....
Grade ($\frac{3}{4}$, slack, nut, run-of-mine, etc.).....
Remarks (appearance of coal, lumps, slate, sulfur balls, weather conditions, etc.).....
Sold by.....Mined by.....
County.....State.....Mine.....

REFERENCE.—This is essentially the Standard Method of the American Society for Testing Materials, adopted 1916, Serial D21-16.

COAL

Proximate Analysis

Preparation of Laboratory Sample.—*When Coal Appears Dry.*—If the sample is coarser than 4-mesh ($\frac{3}{16}$ inch) and larger in amount than 10 pounds, quickly crush it with a jaw crusher to

pass a 4-mesh sieve and reduce by a riffle to between 5 and 10 pounds. Then grind the whole sample to 20-mesh size. If moisture is of special importance, remove about 60 grams immediately with a spoon from various parts of the sample and place at once in a dry rubber-stoppered bottle. This sample is to be used for the determination of total moisture.

Thoroughly mix the main portion of the sample, reducing on a small riffle to about 120 grams, and pulverize to 60-mesh. If desired, this 60-mesh sample may be further reduced by a small riffle to 2–3 ounces.

The sample will become partly dry on grinding, hence if moisture is important, compute the analysis of the 60-mesh sample to the "bone-dry" basis by dividing each result by 1 minus the moisture content expressed as a decimal. Compute the analysis of the coal "as received" from the bone-dry analysis by multiplying each figure by 1 minus the total moisture found in the larger 20-mesh sample, also expressed as a decimal.

When Coal Appears Wet.—Spread the whole sample on weighed pans; weigh quickly and air-dry in a special drying oven at 10–15° C. above room temperature. Continue drying until the loss in weight is not more than 0.1% per hour. Then finish sampling as above under dry coal. When moisture is important correct the moisture found in the 20-mesh air-dried sample to total moisture "as received" as follows:

$$\frac{100 - \text{percentage air-drying loss}}{100} \times (\text{percentage } H_2O \text{ in 20-mesh}) + (\text{percentage air-drying loss}) = (\text{total moisture as received}).$$

Compute the analysis to the bone-dry basis and the "as-received" basis as under dry coal above, using for the "as-received" computation the total moisture as found by the above formula in place of the moisture found in the 20-mesh coal.

NOTES.—(1) In the general run of coal analysis the actual moisture is not important, as must purchases are based on bone-dry figures. In such cases it is not necessary to take a special 20-mesh sample, but wet coal should always be air-dried before grinding. In the latter case the formula for correcting to total moisture "as received" becomes

$$\frac{100 - \text{percentage air-drying loss}}{100} \times (\text{percentage } H_2O \text{ in 60-mesh sample}) + (\text{percentage air-drying loss}).$$

(2) Freshly ground or wet coal loses moisture rapidly, hence sampling operations between opening the container and taking the 20-mesh total moisture sample must be conducted as quickly as possible with very little exposure to air.

(3) The accuracy of the method of preparing laboratory samples should be checked frequently by resampling rejected portions and preparing a duplicate sample. Ash determinations on the two samples should not differ more than the following limits:

	Per cent
No carbonate present	0.4
Considerable carbonate and pyrite present	0.7
Ash over 12% (containing considerable carbonate and pyrite)	1.0

Moisture.—Weigh approximately 1 gram of the 60-mesh sample quickly and accurately in a 15-cc. weighed platinum crucible with tight-fitting capsule cover, previously heated and cooled in a desiccator over conc. H_2SO_4. Keep the crucible covered while weighing the sample. Place in the special moisture oven with cover removed and dry for exactly 1 hour at 104–108° C. Remove and place the crucible with tight-fitting cover in a desiccator over conc. H_2SO_4. When cool, immediately weigh the covered crucible. Report the loss of weight as Moisture.

NOTES.—(1) In determining moisture on the 20-mesh sample, weigh out 5 grams with an accuracy of 0.002 gram and dry for 1.5 hours.

(2) The moisture determination is made in a specially designed double-walled oven. The space between the walls is filled with a glycerin-water mixture of such strength that the boiling point is between 104° C. and 108° C.* Concentration of the solution is prevented by means of a reflux condenser fitted into the top of the oven. Air is pre-dried by passing it through conc. H_2SO_4 at such a rate that the air is renewed in the oven 2–4 times a minute. The pre-dried air is then led through a coil of block-tin tubing which passes through the heated solution of glycerin and water. Air is thus pre-heated before entering the oven. It escapes by means of a small orifice in the door of the oven.

(3) Permissible tolerances:

	Same analyst, per cent	Different analysts, per cent
Moisture under 5%	0.2	0.3
Moisture over 5%	0.3	0.5

* A solution of sp. gr. 1.135 at 60° F. should have the proper boiling point.

Ash.—Place the crucible containing the dried coal from the moisture determination (60-mesh sample) in a cold muffle furnace, or on the hearth of the furnace at low temperature, and gradually heat to redness at such a rate as to avoid mechanical loss from too rapid expulsion of volatile matter. Continue the ignition to constant weight (within 0.001 gram) at a temperature between 700 and 750° C. Cool in a desiccator and weigh as soon as cool.

NOTES.—(1) Before placing the crucible in the muffle for ignition to constant weight, stir the ash with a platinum or nichrome wire. Stirring the ash once or twice before the first weighing hastens complete ignition.

(2) The result thus obtained is "uncorrected ash" and is the ash percentage always reported unless otherwise specified. The actual mineral matters in the original coal are usually quite different in weight and composition from the weight of the uncorrected ash.

(3) High-ash coals require longer heating than low-ash coals.

(4) Permissible tolerances:

	Same analyst, per cent	Different analysts, per cent
No carbonate present	0.2	0.3
Carbonate present	0.3	0.5
More than 12% ash, containing carbonate and pyrite	0.5	1.0

Volatile Matter.—Weigh 1 gram of the 60-mesh sample quickly and accurately in a 15-cc. weighed platinum crucible similar to that used for the moisture determination. Place on a nichrome wire triangle and heat for exactly 7 minutes over a Tirrill burner burning artificial gas.* The temperature at the bottom of the crucible must be regulated by means of a thermo-couple so that it is maintained at 950° C. (±20° C.). Burner and crucible are protected by a cylindrical windshield.

After the more rapid discharge of volatile matter has subsided, as shown by the disappearance of the luminous flame, tap the cover lightly to seal the crucible more perfectly and guard against admission of air. After heating exactly 7 minutes, remove the crucible and let it cool without disturbing the cover. Weigh as soon as cool. The loss of weight, minus the moisture, is the volatile matter.

* The A. S. T. M. Standard D22-21 specifies a vertical electric tube for this test, but we have found a Tirrill burner to give satisfactory results if directions are carefully followed.

NOTES.—(1) *Modification for Sub-bituminous Coal, Lignite, and Peat.*—Mechanical losses are incurred on suddenly heating peat, sub-bituminous coal, and lignite. They must therefore be subjected to a preliminary gradual heating for 5 minutes. This is best done by playing the flame of a burner upon the bottom of the crucible in such a manner as to bring about the discharge of volatile matter at a rate not sufficient to cause sparking. After the preliminary heating, transfer the crucible to the volatile-matter burner and heat for 6 minutes at 950° C., as in the regular method.

(2) The cover of the crucible should fit closely enough so that the carbon deposit from bituminous and lignite coals does not burn away from the under side.

(3) The regulation of temperature to within the prescribed limits is important

(4) Permissible tolerances:

	Same analyst, per cent	Different analysts, per cent
Bituminous coals	0.5	1.0
Lignites	1.0	2.0

Fixed Carbon.—Calculate the fixed carbon by subtracting the percentages of moisture, ash and volatile matter from 100%.

Sulfur (Eschka Method).—Weigh 1.373 grams of the 60-mesh sample and thoroughly mix on glazed paper with 3 grams of Eschka mixture. Transfer the uniform mixture to a 30-cc. Coors glazed-porcelain crucible and cover with about 1 gram of Eschka mixture.

Place the crucible in a cold muffle and gradually raise the temperature to 870–925° C. (cherry-red heat) in about 1 hour. Maintain the maximum temperature for about 0.5 hour and then let the crucible cool in the muffle. When burning is complete, all trace of black coal will have disappeared and only a light, reddish gray mass remains. Make sure such is the case.

When cool, empty the contents into a 200-cc. beaker and digest with 100 cc. of hot water on the hot plate for 30–45 minutes with occasional stirring. Then filter through a rapid 11-cm. filter paper and wash the insoluble matter by decantation. After several washings in this manner, transfer the insoluble matter to the filter and wash five times with hot water, keeping the mixture well agitated. Treat the filtrate, amounting to about 250 cc., with 10–20 cc. of saturated bromine water, make slightly acid with conc. HCl (5 cc.) and boil to expel liberated Br. Make sure the solution is acid by testing with methyl orange. Exactly neutralize with NaOH or Na_2CO_3 solution, then add 2

cc. of 0.5 N HCl. Add slowly from a pipette, with constant stirring, 10 cc. of a 10% solution of $BaCl_2 \cdot 2H_2O$. Continue boiling for 15 minutes and let stand overnight just below the boiling point. (If the analysis is urgent, boil for 30 minutes and let stand 1 hour.)

Filter through an ashless 11-cm. filter paper and wash with hot water until a few drops of the filtrate show no precipitate with $AgNO_3$ solution. Place the wet filter containing the $BaSO_4$ in a weighed alundum (No. 0 or 00) or platinum crucible, allowing free access of air by folding the paper over the precipitate loosely to prevent spattering. Place in a cold muffle and smoke off the paper gradually. At no time let it burn with a flame. After the paper is practically consumed, raise the temperature to approximately 900° C. and heat until the weight is constant after cooling in a desiccator. Calculate to sulfur.

CALCULATION.—Grams of $BaSO_4 \times 10$ = percentage of sulfur.

NOTES.—(1) Always run a blank determination with each analysis, using the same amounts of all reagents that were employed in the regular determination. Deduct the sulfur found in the blank from the amount found in the sample.

(2) Examine the residue of Eschka mixture for sulfur after digesting, by dissolving it in HCl and treating with bromine water and $BaCl_2$. When an appreciable amount of sulfur is found, add it to the main precipitate.

(3) Determinations of ash in coal or coke must not be made in the same muffle at the same time with sulfur determinations.

(4) *Reagents and Solutions.*—Eschka Mixture: Mix 2 parts by weight of light calcined MgO and 1 part by weight of anhydrous Na_2CO_3. Both materials should be free as possible from sulfur. Grind the materials together and after thoroughly mixing pass through an ordinary flour sieve. Keep the mixture in a glass-stoppered bottle.

Saturated Bromine Water: Add excess of bromine to 1000 cc. of water and mix.

Barium Chloride Solution: Dissolve 100 grams of $BaCl_2 \cdot 2H_2O$ in water, and dilute to 1000 cc.

(5) Permissible Tolerances:

	Same analyst, per cent	Different analysts, per cent
Sulfur under 2%	0.05	0.10
Sulfur over 2%	0.10	0.20

REFERENCE.—The procedures in this method are essentially those of the American Society for Testing Materials described in its Book of Standards.

COAL

Heating Value

General.—The common unit for measuring heat is the British Thermal Unit, usually written B.t.u. It is the quantity of heat required to raise 1 pound of water from 62 to 63° F. In the metric system the unit is the Calorie,* the amount of heat required to raise 1 kilogram of water from 15 to 16° C. The relation between the two is therefore:

$$1 \text{ Calorie} = \tfrac{9}{5} \times 2.2046 = 3.9683 \text{ B.t.u.}$$

Since, however, heating values in B.t.u. are usually expressed per pound of material, and in calories are expressed per kilogram or per gram, the relation becomes:

$$\text{(large) Calories per Kg.} \times \tfrac{9}{5} = \text{B.t.u. per pound,}$$
$$\text{or, (small) calories per gram} \times \tfrac{9}{5} = \text{B.t.u. per pound.}$$

In making calorimetric determinations on fuels all figures should be expressed in calories and the final corrected result multiplied by 1.8 to convert to B.t.u. per pound.

Apparatus.—*Combustion Bomb.*—Various bombs may be used for this determination but they must have an inner surface of platinum, gold or some material not attacked by HNO_3, H_2SO_4, or other products of combustion. In this laboratory we use an Emerson Bomb Calorimeter with gold lining.

Calorimeter Jacket.—The calorimeter must be provided with a water-jacket having a cover to protect it from air currents and the jacket must be kept filled with water within 2 or 3° C. of room temperature and the water continuously stirred by a mechanical stirring device.

Stirring of Calorimeter Water.—The water in the calorimeter must be stirred sufficiently to give consistent thermometer readings while the temperature is rising rapidly. The stirrer must not touch the bomb. The speed of stirring must be kept constant and should not be excessive. This may be determined by adjusting the temperature of the calorimeter equal to that of

* This is the "kilogram calorie," written with a capital "C." The small calorie or "gram calorie," written with a small "c," is the amount of heat required to raise 1 gram of water from 15 to 16° C. and is therefore one-thousandth of a Calorie.

the jacket and letting the stirrer run continuously for 10 minutes. If the temperature of the calorimeter rises more than about 0.01° C. in this length of time, the rate of stirring is excessive. The portion of the stirring device immersed in the calorimeter should be separated from that outside by non-conducting material, such as hard rubber.

Thermometers.—The thermometers used for all temperature observations in calorimetric work should be graduated to at least 0.01° C. and calibrated by the U. S. Bureau of Standards. They should be used with the corrections given on the certificate. The thermometer should be tapped lightly just before each reading to avoid errors caused by the lag of the mercury, especially on falling temperature. Read thermometer observations to 0.001° C. with a special reading telescope.

Oxygen.—The oxygen used for combustion must be free from combustible matter.

Firing Wire.—The coal in the bomb may be ignited by means of either iron or platinum wire. In this laboratory we use iron wire No. 34 B & S gage. Not more than 4 inches of wire should be used. Its heat of combustion must be subtracted from the final result. $3\frac{1}{8}$ inches (8 cm.) is a convenient length and this length of No. 34 iron wire has a heating value of 14 calories.* (If any wire is found to be unburned after the combustion it must be deducted from the total amount of wire used.)

Standardization of Calorimeter.—The accuracy of all calorimetric determinations depends upon the correct determination of the water-equivalent value of the apparatus. Standardize the apparatus by means of Naphthalene and Benzoic Acid, the heats of combustion of which have been determined by the U. S. Bureau of Standards. The pure substances should show the following heating values:

Naphthalene.....9622 Calories.†
Benzoic Acid.....6329 Calories.

The determination is made under exactly the same conditions as in the determination on coal. Instead of using 1 gram of

* The exact heating value should be figured from the weight of wire used on the basis of 1600 calories per gram of wire burned.

† In the calculations use the Bureau of Standards' values as given on the bottles, if they differ from these figures.

naphthalene or benzoic acid, however, as in the case of coal, take the following weights:

Naphthalene.....0.8450–0.8550 gram.
Benzoic Acid.....1.2850–1.2950 grams.

Make a pill of naphthalene of the above weight and immediately weigh it accurately and place in the bomb. Also make the benzoic acid into pills, but place these pills in a desiccator over conc. H_2SO_4 for about 8 hours. Then take the required weight and place immediately in the bomb.

CALCULATION.—Let a = Weight of material multiplied by its heating value in calories;
b = Heating value of iron wire in calories;
c = Heating value of titer in calories;
d = Corrected rise in temperature, ° C.;
e = Weight of water in grams;
and g = Water equivalent of apparatus in grams;

$$\text{then } g = \frac{a+b+c}{d} - e.$$

The average of the naphthalene and benzoic acid results should agree within approximately 2 grams. Take for the water equivalent in grams of the apparatus the average of the results by naphthalene and by benzoic acid.

The final water-equivalent *factor* in calories is the water equivalent in grams plus the weight of water in grams. This factor is to be used for converting the corrected temperature rise of the coal to calories. (Calories $\times 1.8$ = B.t.u. per pound.)

Determination of B.t.u.—*Preparation of Sample.*—Mix the finely ground (60-mesh) sample in the bottle and accurately weigh approximately 1 gram into the fuel tray lined with recently ignited asbestos. Bituminous coal may be used directly in the powdered form or in the form of a briquette. If trouble is experienced from blowing out of the crucible, the coal should be briquetted. Anthracite coals and coke do not give this trouble.

Preparation of Bomb.—Measure the firing wire, coil it in a small spiral and connect between the platinum terminals, using, if necessary, a piece of platinum wire somewhat heavier than the iron wire to make the connection. Both the platinum and the iron

must be clean. Place 1 or 2 cc. of water in the bottom of the bomb to saturate with moisture the oxygen used for the combustion. When the fuel tray is put in place in the bomb, the firing wire should be in contact with the sample but *must not* touch the fuel tray.

Filling Bomb with Oxygen.—Screw the lid down against the lead gasket.* Then force oxygen into the bomb very slowly, to avoid blowing the coal from the tray, until the pressure within registers 20 atmospheres (300 pounds). At this point close the needle-point valve just tight enough to prevent leakage of gas.

Calorimeter Water.—Fill the calorimeter with exactly 1900 grams of distilled water, which is the amount specified for the Emerson calorimeter. (The same amount must be used in standardizing the apparatus.)

Temperature Adjustment.—The initial temperature in the calorimeter should be so adjusted that the final temperature after the combustion will not be more than 1° C. (preferably about 0.5° C.) above that of the jacket, under which conditions the total correction for heat gained from or lost to the surroundings will be small when the rise of temperature is 2 or 3° C., and the effect of evaporation loss will be small. (Under normal conditions this is obtained by having the water about 4° C. below room temperature. In the case of anthracite screenings and fuels whose heating value is low, the temperature of the water should be about 3.5° C. below room temperature.)

Firing Current.—The electric current used for firing the charge should be obtained from storage or dry cells having an e.m.f. not greater than 12 volts, since a higher voltage is likely to cause an arc between the firing terminals, introducing additional heat. A suitable current may also be obtained by placing two 100-watt lamps (connected in parallel) in series with the fuse wire on a 110-volt lighting circuit. The circuit should be closed by means of a switch, which should remain closed for not more than 2 seconds.

Determination.—When ready for firing, place the bomb in the calorimeter, connect the current terminals, cover the calorimeter jacket, attach the stirring device and insert the thermometer,

* In handling the bomb take care not to tip or jar it, as fuel may be thrown from the tray.

which must not be within 0.5 inch of the bomb or the container. Start the stirrer and after the thermometer reading has become steady (not less than 2 minutes after the stirrer is started, generally 3 or 4 minutes), take temperature readings at 1-minute intervals for 5 minutes. Then fire the charge, noting the exact time of firing. Make temperature observations at intervals described below under Calculation of Results. When the temperature has reached its maximum and is falling uniformly, take a series of readings at 1-minute intervals for 5 minutes, to determine the final cooling rate.

Titration.—After the last reading, take the bomb out of the bucket and reduce the internal pressure to atmospheric pressure by opening the needle-point valve. Remove the lid and very carefully inspect the interior of the bomb for traces of unburned coal or iron wire. If unburned coal is found, the determination is worthless and must be repeated. A correction must be made for the unburned iron wire.* If the combustion appears complete, rinse out the bomb and fuel tray thoroughly with water and titrate the washings with methyl orange and a standard Na_2CO_3 solution of such strength that 1 cc. is equivalent to 0.02173 gram of HNO_3, the heat of formation of which is 5 calories or 9 B.t.u.

Make a further correction of 13 calories or 23 B.t.u. for each percentage of sulfur present, as found by analysis. This corrects for the excess of the difference in the heats of formation of SO_2 and SO_3 over the heat of formation of HNO_3, and also for the Fe present in the coal as pyrite being burned to Fe_2O_3.

Titration Solution.—Dissolve 18.28 grams of pure anhydrous Na_2CO_3 in water and dilute to 1 liter.

Methyl Orange.—Dissolve 1 gram of methyl orange powder in one liter of water.

Calculation of Results.—The following method of calculation is recommended by the American Society for Testing Materials as giving more accurate results than other procedures which have been recommended in the past:

Observe (1) the rate of rise R_1 of the calorimeter temperature in degrees C. per minute for 5 minutes before firing; (2) the time A at which the last temperature reading is made immediately

* See under Firing Wire, previously described.

before firing; (3) the time B when the rise of temperature has reached six-tenths of its total amount. (This point can generally be determined by adding to the temperature observed before firing 60% of the expected temperature rise* and noting the time when this point is reached); (4) the time C of a thermometer reading taken when the temperature change has become uniform some 5 minutes after firing and (5) the final rate of cooling R_2 in degrees per minute for 5 minutes. Multiply R_1 by the time $B-A$ in minutes and tenths of a minute and add this product (subtract it if the temperature was falling at the time A) to the thermometer reading taken at the time A. Multiply R_2 by the time $C-B$ and add this product (subtract it if the temperature was rising at the time C and later) to the thermometer reading taken at the time C. The difference of the two thermometer readings thus corrected, provided the corrections of the thermometer certificate have already been applied, gives the total rise of temperature due to the combustion. This, multiplied by the water equivalent of the calorimeter, gives the total amount of heat liberated. This result, corrected for the heats of formation of HNO_3 (titer correction) and H_2SO_4 (calculated from the percentage of sulfur) and for the heat of combustion of the firing wire, is divided by the weight of the charge to find the heat of combustion in calories per gram of the sample. This multiplied by 1.8 gives the B.t.u. per pound (see following example).

EXAMPLE:

Observations

Water equivalent = 450.5 grams
Water-equivalent factor = 2350.5 calories

* When the temperature rise is not approximately known beforehand, it is only necessary to take thermometer readings at 40, 50, 60 seconds (and possibly 70 seconds with some calorimeters) after firing, and from these observations to find when the temperature rise has reached 60% of the total. Thus, if the firing temperature was 2.135°; at 40 seconds, 3.05°; at 50 seconds, 3.92°; at 60 seconds, 4.16°; and the final temperature was 4.200°; the total rise was 2.07°, and 60% of it was 1.24°. The temperature to be observed was then $2.14°+1.24°=3.38°$. Referring to the observations at 40 and 50 seconds, the temperatures were respectively 3.05 and 3.92°. The time corresponding to the temperature of 3.38° was therefore

$$40+\frac{(3.38-3.05)}{(3.92-3.05)}\times 10=44 \text{ seconds.}$$

Weight of sample = 1.0240 grams
Approximate rise expected = 3.3°
60% of approximate rise = 2.0°

Time	Readings	Readings corrected for thermometer certificate
3:20 p.m.	16.244°	
21	.250	
22	.255	
23	.261	
24	.266	
(*A*) 25	.272	16.276°
Charge fired		
(*B*) 26.2	18.3*	
(*C*) 30	19.605	19.604
31	.603	
32	.600	
33	.599	
34	.598	
35	.597	

Calculations

$R_1 = 0.028 \div 5 = 0.0056°$ per minute. $B - A = 1.2$ minutes
Corrected initial temperature $= 16.276 + (0.0056 \times 1.2) = 16.283°$
$R_2 = 0.008 \div 5 = 0.0016°$ per minute. $C - B = 3.8$
Corrected final temperature $= 19.604 + (0.0016 \times 3.8) = 19.610°$
Total rise $= 19.610° - 16.283 = 3.327°$

Total calories developed $= 2350.5 \times 3.327 =$	7820
Corrections: Titer (32) + wire (14) + sulfur (33) =	79
Calories from 1.0240 grams of coal =	7741
B.t.u. per pound $= \frac{7741}{1.0240} \times 1.8 =$	13607

NOTES.—(1) *Permissible tolerances:*

Heating value, B.t.u.	Same analyst	Different analysts
12,000	36	60
13,000	39	65
14,000	42	70
15,000	45	75

* The initial temperature is 16.27° and 60% of the expected rise is 2.0°. The reading to observe therefore is 18.3°.

(2) In practice, the time $B-A$ will be found so nearly constant for a given calorimeter with the usual amounts of fuel that it need be determined only occasionally.

(3) The method of computing the cooling correction described in *Bur. Mines Tech. Paper* No. 8, 28–32, may be used in place of the above if desired.

(4) For details of construction of the calorimeter and precautions as to its use, see pamphlet supplied with the calorimeters from the Emerson Apparatus Company.

(5) *"H" Value:* If it is assumed that the calorific value of coal is due to combustion of organic matter and sulfur, it would seem probable that in coals of like character the calorific value would be proportional to the amount of these substances present. Therefore, if the sum of the percentages of moisture, ash and sulfur be subtracted from 100, the remainder would be approximately the organic matter in the coal; and if the calorific value of the sulfur be subtracted from the calorific value of the coal as determined, the remainder should be the calorific value of the organic matter present. The calorific value of coal calculated on a moisture-ash-sulfur-free basis is commonly designated as "H." This "H" value differs for different grades of coal but for the same kind of coal from the same seam is fairly constant. The value of "H," being known for various grades of coals, serves as an approximate check on the analysis.

Calculation of "H."—Let A = B.t.u. as determined;
B = percentage of sulfur expressed as decimal;
C = percentage of moisture expressed as decimal;
and D = percentage of ash expressed as decimal;

$$\text{then "H"} = \frac{A-4050B}{1-(B+C+D)}.$$

Reference.—The procedures in this method are essentially those of the American Society for Testing Materials described in its Book of Standards.

COAL

Ultimate Analysis

Apparatus and Chemicals.—(*a*) The combustion is made in a 25-burner *combustion furnace* of the Glaser type.

(*b*) *The purifying trains* through which the air and oxygen are passed before they enter the combustion tube are arranged in duplicate, one part for air, the other for oxygen, both being connected to the combustion tube by means of a Y-tube. The purifying reagents, arranged in the order of the flow of oxygen or air through them, are: (1) conc. H_2SO_4, (2) 30% KOH solution, (3) soda-lime, and (4) granular $CaCl_2$.

The oxygen and air are allowed to bubble through about 0.25 inch of the reagents (1) and (2), which are in gas-washing bottles. Reagents (3) and (4) are in U-tubes.

(*c*) *The combustion tube* is about 40 inches long and about $\frac{5}{8}$ inch (16 mm.) internal diameter, made of hard glass or silica. The tube extends beyond each end of the furnace for a distance of about 4 inches, the ends of the tube being protected from the heat of the furnace by closely fitting circular shields of asbestos. The rear end of the tube (the end next to the purifying train) is closed with a rubber stopper. As this end of the tube is kept cool by the protection of the circular shield and by the passage of cool air and oxygen, there is very little danger of volatile products being given off by the rubber. The other end of the tube is closed by a well-rolled cork of specially selected quality, the danger from overheating at this end of the tube being too great to permit the use of the more convenient rubber stopper.

The tube is filled as follows: A space of 5–5.5 inches is left empty at the end nearest the absorbing train. Then follow: (1) a plug of asbestos; (2) 4–5 inches of fused $PbCrO_4$ in small lumps; (3) an asbestos plug; (4) 14–16 inches of pure, recently ignited "wire" CuO (or a close coil of fine copper gauze thoroughly oxidized by heating it in a stream of pure oxygen); (5) an asbestos plug; (6) the boat for holding the coal. There must be 12 14 inches of empty tube following the last asbestos plug, so that the part of the tube in which the boat is placed will be well in the furnace, and yet the tube itself project at least 4 inches outside of the furnace.

(*d*) *The absorption train* is as follows: The water is absorbed in a 6-inch U-tube, filled with granular $CaCl_2$; the CO_2 is absorbed by KOH (30% solution *) in an ordinary Liebig bulb, to which is attached a 3-inch U-tube containing soda-lime and granular $CaCl_2$, the bulb and U-tube being weighed together. This is followed by a final guard tube filled with $CaCl_2$ and soda-lime to prevent any back-pressure of CO_2 or H_2O. The gases formed during combustion are drawn through the train by suction, a Marriott bottle being used to secure a constant suction head.

(*e*) *The oxygen* used is kept over water and is supplied under small pressure. The supply of oxygen and the aspiration during

* To this should be added a little $KMnO_4$ to oxidize any possible oxidizable impurities.

a combustion are so regulated as to keep the difference in pressure between the inside and outside of the tube very small, the pressure inward being slightly greater. This reduces the danger of leaks to a minimum, and, if by chance any slight leakage does occur, it is inward rather than outward and the effect upon the determination is small.

Testing the Apparatus.—Before beginning the determination test the apparatus for leaks by starting the aspirator at the rate of 3 bubbles of air per second through the KOH bulb and then shutting off the supply of air. If not more than 1 bubble of air per minute passes through the KOH bulb, the connections are sufficiently tight to proceed with the determination. Air is then admitted to the purifying apparatus, the tube heated to redness throughout and 1000 cc. or more of air aspirated. The KOH bulb and drying tube are then detached and weighed. They are again connected up and 500 cc. of oxygen, followed by 1000 cc. of air, are aspirated through the train.

On commencing the second aspiration, the burners under the rear portion of the tube are gradually turned down and finally entirely out, so that the empty portion of the tube into which the sample for analysis is to be inserted becomes nearly or quite cool by the time the aspiration is complete. The burners under the two-thirds of the CuO next to the $PbCrO_4$ are kept lighted and this portion of the CuO kept at a red heat. After aspiration of the 1000 cc. of air, the KOH bulb and drying tube are detached and again reweighed. If the gain or loss in weight is less than 0.0005 gram, the apparatus is ready for an analysis.

Carbon and Hydrogen.—Ignite and cool the boat. Weigh it empty in a glass-stoppered weighing bottle. Place in it about 0.2 gram of the finely pulverized and well-mixed air-dry coal. (The sample must be ground very fine, otherwise, in weighing so small a quantity, average results will not be obtained.) Place the boat in the bottle, quickly stopper and weigh accurately. Insert the boat quickly into its proper place in the combustion tube and connect up the apparatus.

The tube should be cool after the first 12 inches, the CuO should be red hot and the $PbCrO_4$ at a dull red heat.* The boat

* When silica tubes are used, the $PbCrO_4$ section should be kept slightly below even a dull red on account of danger of fusing the tube.

should be transferred from the weighing bottle to the combustion tube as rapidly as possible to avoid change in moisture content and should be placed near the asbestos plug at the beginning of the CuO section.

After connecting up the apparatus, start the aspiration with pure oxygen at the rate of 3 bubbles per second. Turn on 1 burner about 4 inches back from the boat and continue aspiration carefully until practically all moisture is expelled from the sample. Then increase the heat very gradually until all the volatile matter has been driven off. In doing this, the heat must be applied gradually in order to prevent a too rapid evolution of gas and tar which might either escape complete combustion or be driven back into the purifying train. The heat should be slowly increased by turning on more burners under the open part of the tube until the sample is ignited; then increase the temperature rapidly, taking care, however, not to melt the combustion tube. Drive over into the $CaCl_2$ tube any moisture collecting in the end of the combustion tube or in the rubber connection joining it to the $CaCl_2$ tube, by carefully warming with a piece of hot tile. Continue the aspiration with oxygen for 2 minutes after the sample ceases to glow, then turn off the heat and aspirate about 1200 cc. of air through the tube. Finally, disconnect the absorption bulbs, wipe with a clean cloth, cool in the balance room until they come to room temperature and then weigh. Calculate the percentages of carbon and hydrogen by the following formulas:

$$\% \text{ C} = 27.28 \times \frac{(\text{increase in weight of KOH bulb})}{\text{Weight of sample}}.$$

$$\% \text{ H} = 11.19 \times \frac{(\text{increase in weight of } CaCl_2 \text{ tube})}{\text{Weight of sample}}.$$

NOTES.—(1) The percentage of H as calculated contains the H of the moisture in the sample. To correct for this subtract one-ninth of the percentage of moisture found by a separate determination.

(2) After the boat has been removed, the apparatus is ready for another determination, since any CuO will all have been reoxidized by the air current.

(3) After removing the boat, weigh the ash (unless the ash has been determined on another sample) and carefully inspect it for any unburned carbon. If such is found, the determination is worthless and must be repeated.

(4) The wire CuO should be used, as the ordinary granular oxide sometimes contains carbon and carbonates. It should be examined for $CaCO_3$ or other carbonates which are likely to give off CO_2 on heating, and also for

lime which may absorb CO_2. The CuO may be tested for CaO by extracting it with a little dil. HNO_3, adding NH_4OH in excess and then testing the liquid with $(NH_4)_2C_2O_4$. It should give no precipitate.

(5) The asbestos used should be boiled in HCl, washed, dried and ignited, in order to remove traces of $CaCO_3$ or other carbonates sometimes present.

(6) The $PbCrO_4$ should be in moderately coarse lumps from which all fine material has been sifted out with a 20- or 30-mesh sieve. It must be neutral and free from alkaline chromates. The same $PbCrO_4$ can be used for many determinations; as long as it does not turn green for more than 20% of its length in the tube, it is perfectly safe.

(7) The oxygen should be tested as to its purity and must *not* be kept in rubber bags or passed through long rubber tubes.

(8) Check determinations should agree within 0.07% for H, 0.30% for C and 0.05% for N.

Nitrogen.—Weigh 1 gram of the finely pulverized coal into a Kjeldahl distilling flask and determine the nitrogen by the Gunning method as described on page 88.

Sulfur.—Determine the sulfur as described on page 215.

Oxygen.—As no satisfactory method is known for the direct determination of the oxygen in coal, it is always determined "by difference," the sum of the percentages of H, C, N, S, moisture and ash being subtracted from 100% and the remainder called oxygen. The result so obtained is always inaccurate, the error increasing with the percentages of ash and sulfur. The weight of the ash does not represent that of the mineral matter in the coal, the pyrite in the coal being burned to Fe_2O_3 and the sulfur passing off as SO_2. Thus 4 atoms of S in 2 FeS_2 are replaced by 3 atoms of O in the Fe_2O_3, and the loss of weight is equal to five-eighths of the S. For this reason many chemists use five-eighths of the S, instead of the total S found by analysis, in calculating the O. As coals contain sulfur in other forms than FeS_2, however, and also frequently other compounds that lose weight on burning, such as $FeCO_3$ and $CaCO_3$, it is doubtful whether the results obtained in this way are any closer to the truth.

REFERENCES.—Lord: "Notes on Metallurgical Analysis," 165–170. *Bull.* 9, *Geol. Survey of Ohio*, 317–319; *U. S. Dept. Agr., Div. Chem., Bull.* 46, Revised, 14–16 (1899); *Am. Soc. Testing Materials*, "Triennial Standards" (1924), 1000.

PHOSPHORUS IN COAL AND COKE

Ignite to ash in a platinum crucible exactly 10 grams of coal or 5 grams of coke. Add 15 cc. of conc. HNO_3 and about 5 cc. of

HF. Evaporate carefully to dryness under a good hood. Fuse the residue with 3 grams of Na_2CO_3 (if any unburned carbon is present in the ash, 0.2 gram of $NaNO_3$ should be mixed with the Na_2CO_3). Leach out the melt with water, filter and wash. Ignite the residue and again fuse with Na_2CO_3. Leach out this melt, filter and wash. Acidify the combined filtrates in a flask with a very slight excess of HNO_3 and concentrate to a volume of 100 cc. Neutralize with conc. NH_4OH and add approximately 5 cc. in excess. Then make slightly acid with HNO_3, bring the solution to a temperature of 80° C., add 60 cc. of ammonium molybdate solution and shake for 5 minutes. Complete the determination as under Phosphorus in Steel (p. 138), dissolving the yellow precipitate in standard NaOH solution and titrating the excess with standard HNO_3 solution.

Reference—This method is similar to that of the *Am. Soc. Testing Materials*, "Triennial Standards," 993, (1924).

COAL-ASH AND REFUSE

General.—The usual determinations on samples of coal-ash or refuse are percentages of moisture, combustible matter and ash, and calculation of the B.t.u. per pound.

Moisture.—Dry 1 gram of the finely powdered sample in a weighed platinum crucible for 1 hour at 110° C., in the special water-glycerin oven described on page 213.

Ash.—Ignite the residue from the above moisture determination in the platinum crucible in a muffle at approximately 900° C., until complete combustion is obtained. Cool in a desiccator and weigh.

Combustible Matter.—Subtract from 100% the percentages of moisture and ash as above determined. The difference is combustible matter.

B.t.u. per Pound.—Calculate the heating value on the arbitrary basis of 14,600 B.t.u. per pound of combustible matter. In other words, multiply the percentage of combustible matter, expressed as a decimal, by 14,600.

Note.—It is often customary to report results on the dry basis. In such case divide the results obtained for combustible, ash, and B.t.u., respectively, on the "as-received" basis by the difference between 1.0000 and the moisture

percentage expressed as a decimal. In the case of very wet samples, requiring preliminary air-drying, proceed as under Coal (p. 212).

GASOLINE

General.—The essential desirable properties in gasoline for motor use are:

1. It should not contain too large a percentage of highly volatile products which tend to cause large evaporation losses and excessive danger in handling and storage, but should have sufficient volatile constituents to permit starting an engine under reasonably unfavorable conditions without pre-heating.

2. It should not contain any considerable percentage of heavy or non-volatile constituents which, after atomization into the engine cylinders, cannot be completely vaporized and burned.

3. It should not contain any material which, after combustion, leaves a residue which collects in the motor.

4. It should be free from substances which attack metal, either before or after combustion. This includes unremoved acid used in refining.

5. Neither the gasoline nor its products of combustion should have a strong or markedly disagreeable odor.

6. It should be free from non-combustible material such as water, sediment, etc.

Types of Gasoline.—1. *"Straight" Refinery Gasoline.* In general these are made by distilling crude oil in a fire still and taking a cut when the gravity of the product reaches some predetermined mark. So-called crude naphtha or benzine is acid refined and steam distilled. Several products of different ranges of volatility may be produced, or the steam distillation may simply separate the product from the less volatile bottoms which go into the burning oil stock.

"Straight" refinery gasolines are generally characterized by a low content of unsaturated and aromatic hydrocarbons, and by a distillation range free from marked irregularities.

2. *Blended Casing-head Gasoline.* Casing-head gasoline is obtained from natural gas by compression or absorption. It is too volatile for general use "straight" and, before being marketed, is generally blended with sufficient heavy naphtha. The resulting mixture is characterized in general by a volatility range

showing a considerable percentage of constituents of low and high boiling points, but a lack of intermediate products. Frequently, however, the blending is done in a manner difficult to detect, the natural gas gasoline being used in moderately small proportion with heavy straight-run naphtha in order to make a product having a desirable percentage of volatile constituents.

As regards chemical properties, blended casing-head gasoline seems to be identical with "straight" refinery products of the same distillation range. The characteristic physical properties of blended gasoline are due wholly to the details of blending.

3. *Cracked or Synthetic Gasoline.* These are marketed largely, if not altogether, in the form of blends with "straight" refinery and casing-head gasoline. The cracked gasolines are similar to "straight" refinery products in most physical and chemical properties but contain varying percentages of unsaturated and aromatic hydrocarbons.

Specifications.—The U. S. Government specifications* for gasoline are as follows:

	Aviation gasoline (domestic grade)	Motor gasoline
Color, not darker than	No. 25 Saybolt	No. 16 Saybolt
Doctor test	Negative	.....
Distillation range:		
First drop (maximum)	.....	131° F.
5% (maximum)	167° F.	.....
(minimum)	122° F.	.....
20% (maximum)	.....	221° F.
50% (maximum)	221° F.	284° F.
90% (maximum)	311° F.	392° F.
96% (maximum)	347° F.	.....
End-point (maximum)	374° F.	437° F.
Distillate recovered (minimum)	96%	95%
Distillation loss (maximum)	2%	.....
Acidity (test *b*)	None	.....
Sulfur (maximum)	0.10%	0.10%

When 100 cc. of aviation gasoline are subjected to the copper dish corrosion test it must cause no gray or black corrosion and the amount of deposit in the dish must not exceed 0.003 gram.

* *Bur. Mines Tech. Paper* 323A (March, 1924).

A clean copper strip when submerged in motor gasoline for 3 hours at 122° F. must not discolor.

Water and Foreign Matter.—The sample should be free from water, sediment, and other foreign matter. Water is seldom present and is easy to detect, as an appreciable amount will separate into a lower layer.

Color and Odor.—Properly refined gasolines are water-white and the color of a sample as seen in a 4-ounce sample cylinder should be noted. The sample also should be free from rank and disagreeable odors.

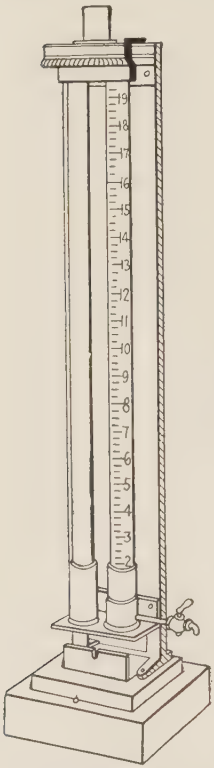


Fig. 11.—Saybolt Chromometer.

The quantitative measurement of the color is made in the Saybolt chromometer (see Fig. 11). This consists of 2 glass tubes of 14–16 mm. internal diameter. One tube is 20 inches long and graduated in $\frac{1}{8}$-inch divisions. The other tube is 19 inches long and fitted with a collar for holding standard color disks. The instrument is provided with an eyepiece and prisms so arranged that light from an artificial daylight lamp, reflected by a mirror up through the tubes in parallel rays, appears on a circular field of vision, the two halves of which are illuminated by the light transmitted by the sample and the color standard, respectively.

In using the instrument, first clean the graduated tube by rinsing with a portion of the sample and allowing it to drain thoroughly. Then fill the tube to a height of 10.5 inches. Use 2 color disks in the other tube, unless the sample appears lighter when viewed in the eyepiece, in which case use 1 disk. Add more of the sample if necessary to make the color distinctly darker than the standard. Then slowly draw down the sample in the graduated tube until it appears slightly darker than the standard. Note the reading and draw down to the nearest height corresponding to a standard color shade as shown in Table VIII. If the color of the sample observed through the eyepiece is still darker than the color standard, again draw down the liquid to

the next height given in the table. Continue the operation until the sample and the color standard match or show questionable differences. Finally lower the liquid one shade more, and if it is then unmistakably lighter than the color standard, record the previous color shade as the Saybolt Color of the sample.

TABLE VIII—COLOR STANDARDS CORRESPONDING TO HEIGHTS OF OIL IN SAYBOLT CHROMOMETER

Number of Disks	Height of Oil, Inches	Color Shade	Number of Disks	Height of Oil, Inches	Color Shade
1	20.0	+25	2	5.50	+4
1	18.0	+24	2	5.25	+3
1	16.0	+23	2	5.00	+2
1	14.0	+22	2	4.75	+1
1	12.0	+21	2	4.50	0
1	10.75	+20	2	4.25	−1
1	9.50	+19	2	4.00	−2
1	8.25	+18	2	3.75	−3
1	7.25	+17	2	3.625	−4
1	6.25	+16	2	3.50	−5
2	10.50	+15	2	3.375	−6
2	9.75	+14	2	3.25	−7
2	9.00	+13	2	3.125	−8
2	8.25	+12	2	3.00	−9
2	7.75	+11	2	2.875	−10
2	7.25	+10	2	2.75	−11
2	6.75	+ 9	2	2.625	−12
2	6.50	+ 8	2	2.50	−13
2	6.25	+ 7	2	2.375	−14
2	6.00	+ 6	2	2.25	−15
2	5.75	+ 5	2	2.125	−16

NOTE.—*Bichromate Control Method.*—For a convenient control method which does not require the use of the Saybolt chromometer, standard acidified $K_2Cr_2O_7$ solutions may be prepared to correspond with the solutions indicated in Table IX. Each of these solutions may be placed in a 4-ounce bottle, marked with the equivalent Saybolt color value, and used for comparison with the same volume of gasoline in a similar 4-ounce bottle.

TABLE IX—BICHROMATE SOLUTIONS CORRESPONDING TO SAYBOLT COLOR VALUES

Saybolt Color	Milligrams of $K_2Cr_2O_7$ per 100 cc. of 1% H_2SO_4
25	0.20
24	0.30
23	0.37
22	0.45
21	0.55
20	0.65
19	0.75
18	0.85
17	0.95
16	1.10
15	1.25
14	1.35
13	1.50
12	1.65
11	1.75
10	1.85
9	1.95
8	2.05
7	2.17
6	2.30
5	2.40
4	2.55
3	2.65
2	2.75
1	2.85
0	3.00

Specific Gravity.—In view of the various sources of gasoline now on the market, the sp. gr. is no longer of any particular value as an index of the quality.* It may be determined with a pyc-

* In spite of this fact, however, it should be remembered that gasoline is bought and sold by the gallon; and the higher the specific gravity, the greater is the weight per gallon and consequently the greater is the fuel value per gallon.

nometer, Westphal balance, or hydrometer. It is customary to express results in terms of Baumé gravity.

Doctor Test.—Shake vigorously together 10 cc. of gasoline and 5 cc. of the "doctor solution" (see below) in a test-tube for about 15 seconds. Add a small pinch of flowers of sulfur, again shake for 15 seconds and let settle. The quantity of S used should be such that practically all the S floats on the surface separating the gasoline from the lower solution.

If the gasoline is discolored, or if the sulfur film is so dark that its yellow color is noticeably masked, report the test as *positive*, condemning the gasoline as "sour." If the sample remains unchanged in color and if the sulfur film is bright yellow or only slightly discolored with gray or flecked with black, report the test as *negative* and the gasoline as "sweet."

"*Doctor Solution*" (*Sodium Plumbite*).—Dissolve approximately 125 grams of NaOH in 1 liter of water. Add 60 grams of PbO and shake vigorously for 15 minutes, or let stand with occasional shaking for at least a day. Let settle and decant or siphon off the clear liquid. If the solution does not settle clear, filter through an asbestos mat. Preserve in a bottle tightly stoppered with a cork. Refilter before use, if not perfectly clear.

Corrosion Test.—(*a*) *Copper Dish.*—Place 100 cc. of the gasoline in a freshly polished hemispherical dish of spun copper, approximately 3.5 inches in diameter. (The dish should be previously weighed if the amount of gummy material is desired.) Place the dish in the opening of an actively boiling steam bath so that the steam comes in contact with the outer surface of the dish up to the level of the gasoline. Leave the dish on the steam bath until all volatile material has disappeared.

If the gasoline contains any dissolved elementary sulfur, the bottom of the dish on the inside will be colored gray or black. If it contains undesirable gum-forming constituents, there will be a weighable amount of gum deposited on the dish. Acid residues will show as gum in this test.

(*b*) *Copper Strip.*—Place a clean strip of mechanically polished pure sheet copper, about 0.5 inch wide and 3 inches long, in a suitable clean tube or sample bottle and add the gasoline so that the Cu strip is completely immersed. Close the container with a loosely fitting cork and hold in a suitable bath at 122° F. At

the end of 3 hours remove the strip and compare it with a similar strip of freshly polished Cu. The presence of free S or corrosive S compounds is indicated by the corrosion or discoloration of the gasoline-exposed strip as compared with the fresh Cu strip. When the exposed strip shows no discoloration, report the gasoline as passing the test.

NOTES.—(1) The Copper-strip Method is A. S. T. M. Method D130-22T. It detects free sulfur and corrosive sulfur compounds.

(2) The Copper-dish Test is recommended for aviation gasoline and the Strip Test for motor gasoline.

Acidity.—(*a*) Shake 10 cc. of the gasoline with 5 cc. of distilled water and test the water with blue litmus paper, which should not turn red. The amount of acid may be determined quantitatively by taking a larger known amount of gasoline and titrating the water with 0.1 N or 0.01 N NaOH and methyl orange.

(*b*) After measuring the residue from distillation (see p. 240) add to it 3 volumes of distilled water and shake thoroughly. Let separate and remove the aqueous layer to a clean tube with a pipette. Add 1 drop of methyl orange indicator solution. No pink or red color should be produced.

NOTE.—Test (*a*) is convenient when no distillation is to be made. Test (*b*), however, is preferable, as the acid is concentrated into a smaller volume.

Distillation.—Conduct the distillation of 100 cc. of the sample in an Engler distilling flask. (In case it is desired to determine the sp. gr. of the different fractions, 200–500 cc. should be employed for distillation.)

APPARATUS.—The apparatus for the distillation (Fig. 12) is as follows:

Flask.—The flask used is the standard 100-cc. Engler flask. The dimensions are as follows:

	Dimensions		Tolerances
	Centimeters	Inches	Centimeters
Diameter of bulb, outside	6.5	2.56	0.2
Diameter of neck, inside	1.6	0.63	0.1
Length of neck	15.0	5.91	0.4
Length of vapor tube	10.0	3.94	0.3
Diameter of vapor tube, outside	0.6	0.24	0.05
Diameter of vapor tube, inside	0.4	0.16	0.05

Position of vapor tube, 9 cm. (3.55 inches) ±3mm. above the surface of the liquid when the flask contains its charge of 100 cc.

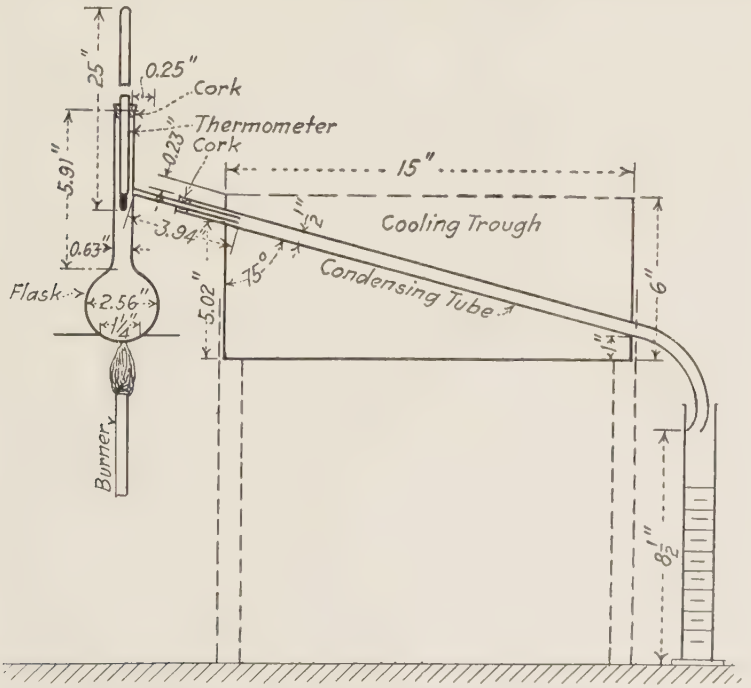


FIG. 12.—Apparatus for Distillation of Gasoline.

The tube is approximately in the middle of the neck and set at an angle of 75 deg. with the vertical.

The flask is surrounded by a shield extending above the side-arm and is supported on a 6×6 inch square of asbestos board having a circular opening 1.25 inches in diameter; this means that only this limited portion of the flask is to be heated. The use of a sand bath is prohibited. The flame of the burner should never be so large that it spreads over a circle of greater diameter than 3.5 inches on the under surface of the asbestos board.

Condenser.—The condenser consists of a thin-walled tube of metal (brass or copper) 0.5 inch internal diameter and 22 inches long. It is set at an angle of 75 deg. from the perpendicular and surrounded with a water jacket of the trough type. The lower end of the condenser is cut off at an acute angle and curved down for a length of 3 inches and slightly backward so as to insure contact with the wall of the graduate at a point 1–1.25 inches below the top. The condenser jacket is 15 inches long.

NOTE.—For ordinary purposes in comparing different samples an ordinary Liebig condenser with an inner tube at least 22 inches long and a 16-inch jacket may be used. The water running through it should be as cold as possible and the graduated cylinder collecting the sample should preferably be surrounded by ice water.

Thermometer.—The accuracy of the distillation primarily depends upon the accuracy of the thermometer. It should be an accurate nitrogen-filled instrument* with a short bulb (10–15 mm. long). The diameter of the thermometer should be between 6–7 mm. and the diameter of the bulb 5–6 mm. The total length should be approximately 380 mm. and the range from 0–300° C. or 30–580° F. The mark for 0° C. or 30° F. should be between 100–110 mm. from the bottom of the bulb, and the top of the stem should be between 30–45 mm. above the 300° C. or the 580° F. mark. It should be scaled for total immersion with an accuracy of 0.5° C. or 1° F. The above requirements insure that nearly always the lowest temperatures registered will come above the cork of the distillation flask and variations because of the stem correction will always be practically the same. The stem correction should not be applied, but it should be understood that results of distillation are expressed in terms of thermometer readings, not of actual temperatures.

* The standard thermometer is the "A. S. T. M. Low Distillation."

PROCEDURE.—Fill the flask, connected to the condenser, with a 100-cc. charge of gasoline, measured from a 100-cc. graduated cylinder at a temperature of 55–65° F. (13–18° C.). Use the same cylinder, without drying, as the receiving vessel for the distillate. Unless the room temperature is between 55–65° F. set the cylinder in a water bath maintained within these limits. Have the end of the condenser tube extend into the cylinder at least 1 inch but not below the 100-cc. mark. Cover the top of the cylinder closely during the distillation with a piece of blotting paper or its equivalent, cut to fit the condenser tube tightly.

Fit the thermometer provided with a cork tightly into the flask so that it will be in the middle of the neck and the lower end of the capillary tube will be on a level with the inside of the bottom of the side-arm tube where it joins the neck of the flask. Have the side-arm extend into the condenser tube between 1 and 2 inches.

Have the condenser trough filled with a mixture of cracked ice and water (not dry cracked ice), and during the distillation keep sufficient ice in the trough to prevent the temperature of the cooling water exceeding 8° C. (40° F.).

Apply heat to the flask at uniform rate so that the first drop of condensate falls from the end of the condenser in not less than 5 nor more than 10 minutes. Record the temperature at which this occurs as the Initial Boiling Point. Then move the graduate so that the end of the condenser touches the side of the graduate and regulate the heat so that distillation proceeds at a uniform rate of not less than 4 nor more than 5 cc. per minute.* Record the temperature when 1 cc. has distilled over, and then continue to take readings at 10, 20, 30, 40, 50, 60, 70, 80, 90, and 95 cc. (or every 5 cc., if desired).

After the 90% point has been recorded, the heat may be increased because of the presence of the heavy ends which have high boiling points. No further increase of heat, however, should be applied after this adjustment. The 4–5-cc. rate can rarely be maintained from the 90% point to the end, but in no case should the period between the 90% and the end-point be more than 5 minutes.

Continue the heating until the mercury reaches a maximum and starts to fall consistently. Record the highest temperature

* This is approximately 2 drops per second.

observed on the thermometer as the Maximum Rise or the End-point. This will usually be reached after the bottom of the flask has become dry.

Record the total volume of the distillate collected in the graduate as the Recovery. Cool the residue in the flask, pour it into a small cylinder, graduated to 0.1 cc., measure when cool and record as the Residue. Calculate the difference between 100 cc. and the sum of the Recovery and the Residue and record it as Distillation Loss. If this is over 3%, make a check distillation, as excessive loss may indicate that the rate of distillation at the beginning was too rapid. In case the magnitude of the loss is confirmed, this fact is of importance in indicating that the gasoline contains very volatile constituents, particularly those derived from adding casing-head gasoline.

If distillations are made at high altitudes or when barometric pressures are low, allowances may be made for this factor. In general, recording the barometric pressure read at the time of the distillation will suffice, and it is recommended that whenever there is possibility of dispute over the results of a distillation this should be done.

NOTES.—(1) *Accuracy.*—With proper care and attention to detail, duplicate results obtained for initial boiling point and maximum temperature, respectively, should not differ from each other by more than 6° F.

(2) The use of apparatus at least approximately as described is essential, although the method is such that no considerable discrepancies will result if the apparatus is not exactly standard. The chief source of difficulty is the rate of heating and the speed should come within the above limits.

(3) *Barometric Pressure.*—If the barometric pressure at the time of distillation varies more than 1 inch (25 mm.) of mercury from the average barometric pressure of the point where the gasoline is delivered to the consumers (as ascertained from records of the U. S. Weather Bureau), corrections in the boiling points should be made according to the following table:

Apparent Boiling Points		Correction
From	To	
57° F.	91° F.	2.9° F.
91	124	3.1
124	158	3.2
158	190	3.4
190	225	3.6
225	239	3.8
239	291	4.0
291	324	4.1
324	358	4.3
358	390	4.5
390	424	4.7
424	457	4.9
457	491	5.0
491	523	5.2
523	558	5.4
558	590	5.6

If the observed barometric pressure is above the average, subtract the above corrections for each inch (25 mm.) of excess pressure; if the pressure is below the average, add the corrections.

Unsaturated Hydrocarbons.—Run 10 cc. of the gasoline from a pipette into a clean, dry Babcock 50% cream bottle. Cool for 2 minutes by immersing in ice water and then add 20 cc. of commercial 66° Bé. H_2SO_4. Let the acid run quietly down the side of the bottle instead of splashing upon the surface of the gasoline. Place a rubber stopper in the bottle and shake the contents, first slowly and then vigorously, with a rotary motion for 5 minutes. Then add conc. H_2SO_4 to the contents of the bottle until the surface of the liquid is just below the upper graduation mark on the neck. Stopper tightly and let stand 12 hours or overnight. Report the percentage loss of volume as Unsaturated Compounds.

If the test is urgent, place the stoppered bottle in a centrifuge and revolve for 2 or 3 minutes at a speed of 500–1000 r.p.m. Then add sufficient acid to bring the level up to the lower graduation mark and again centrifuge. Finally add more acid to bring

the column to the upper graduation mark and read the residual volume of the gasoline.

NOTE.—Each per cent graduation on the Babcock cream bottle is calibrated to 0.2 cc. The reading of the volume of residual gasoline in the bottle should, therefore, be multiplied by 2 to obtain the percentage of residue. This percentage subtracted from 100 gives the percentage of unsaturated hydrocarbons.

Sulfur.—See page 252.

REFERENCE.—*Bureau Mines Tech. Paper* 323A (March, 1924).

FUEL OILS

General.—Fuel oils vary widely in their properties as they not only come from different crude oil sources but also the different crudes may be subjected to various treatments before being marketed as fuel oils. The heavy Mexican fuel oils of high viscosity, high sulfur content and Baumé gravity down to 12° or even lower, are coming into wide use. At the other extreme is the class of gas oils usually running 33–37° Bé. gravity and quite fluid even in cold weather.

Fuel oil usually varies in heating value from 17,500 to a maximum of 20,000 B.t.u. per pound, the average value running about 18,000–19,000.

Most specifications require that fuel oil shall be hydrocarbon oil free from grit, acid and fibrous or other foreign matters likely to plug or injure the burners or valves. Additional requirements of certain common specifications are tabulated below, the figures for Flash Point being minimum allowance and all others maximum:

(*A*) U. S. Government special fuel oil for Diesel engines in submarines.

(*B*) U. S. Navy standard fuel oil.

(*C*) U. S. Government bunker fuel oil A (Low viscosity).

(*D*) U. S. Government bunker fuel oil B (Medium viscosity).

(*E*) U. S. Government bunker fuel oil C (High viscosity).

	A	B	C	D	E
Flash point	150° F.	150° F.*	150° F.*	150° F.	150° F.
Water and sediment	0.2%	1.0%	1.0%	1.0%	1.25%†
Saybolt furol viscosity:					
at 77° F	.....	100	100	.....	.....
at 122° F	.....	.....	.....	100	300
Sulfur	.....	1.5%	.....	.....	.....
Carbon residue	0.5%	.....	.....	.....	.....
Precipitation number	0.5	.....	.....	.....	.....

* In case of oils having a viscosity over 30 at 150° F. (Saybolt furol), the flash shall not be below the temperature at which the oil has a viscosity of 30 seconds.

† Water not over 1%; sediment not over 0.25%.

In the West fuel oil is commonly bought and sold on a Baumé gravity guarantee. A common specification for California fuel oil is as follows:

1. The viscosity must be such that the oil will flow freely through a 4-inch pipe at 70° F.

2. The water content must be less than 2%, using gasoline in the testing flask.

3. The flash test shall not be less than 110° F. (Open Cup).

4. The gravity shall be between 14 and 29° Bé.

5. The oil shall be sold on a 63° F. basis with 1% correction for every 25° F. above or below.

As fuel oils are purchased by the gallon, the purchaser gets more value for oils of low Bé gravity, other things being equal.

The following tests are those usually applied to fuel oils. Where the test is followed by a number, the latter refers to the method number of the Federal Specifications Board as published in Technical Paper 323A of the U. S. Bureau of Mines. Before testing the sample it should be mixed very thoroughly to incorporate with the oil any sediment or moisture that may have settled to the bottom.

Gravity Baumé.—Determine the gravity with a Baumé hydrometer at 60° F. In the case of thick oils it may be necessary to determine the gravity at an elevated temperature and correct the results to 60° F. (see p. 326).

Flash Point (110.21).*—Determine the flash point by the Pensky-Martens closed tester (unless the use of the Tag tester is specified).

Two standard thermometers are supplied with the instrument. Use the low range "P. M. and Tag"† thermometer when the indicated reading falls within the limits 20–200° F. Use the "P. M. High" thermometer for the test when the indicated reading is within the limits 230–700° F. For the range 200–230° F. either thermometer may be used. See that the thermometer is mounted so that the bottom of the bulb is 1.75 inches below the level of the rim of the cup (which corresponds to the level of the lower surface of the portion of the lid inside the rim).

In making the test see that all parts of the cup and its accessories are thoroughly clean and dry before the test is started. Take particular care to avoid the presence of gasoline or naphtha used to clean the apparatus after a previous test. Fill the cup with the oil to be tested up to the level indicated by the filling mark. Place the lid on the cup and set the latter in the stove, taking care to have the locating devices properly engaged. Then insert the thermometer. If the oil is known to flash above 220° F., use the "P. M. High" thermometer, otherwise it is preferable to start with the "P. M. and Tag" thermometer and change in case a temperature of 220–230° F. is reached.

Light the test flame and adjust it so that it is of the size of a bead $\frac{5}{32}$ inch in diameter. Apply heat at such a rate that the mercury column in the thermometer rises not less than 9 nor more than 11° F. per minute and have the stirrer turn at the rate of 1 to 2 revolutions per second.

Apply the test flame at each temperature reading which is a multiple of 2° F. up to 220° F. For the temperature range above 220° F. apply the test flame at each temperature reading which is a multiple of 5° F. The first application of the test flame must be made at least 30° F. below the actual flash point. The application of the test flame is made by operating the device controlling the shutter and test-flame burner so that the flame is lowered

Am. Soc. Testing Materials, Method D93-22.

† This thermometer is the instrument specified for use with the Tag closed tester. (For directions for using the Tag tester see *Am. Soc. Testing Materials*, Standard D56-21.)

in 0.5 second, left in its lowered position for 1 second, and quickly raised to its high position. Discontinue the stirring during the application of the test flame.

Take the flash point as the temperature read on the thermometer at the time of the flame application that causes a distinct flash in the interior of the cup. The true flash must not be confused with the bluish halo that sometimes surrounds the test flame for the applications preceding the one that causes the actual flash.

NOTE.—The barometric pressure should be observed and recorded but no correction is made except in case of dispute, when the flash-point figure is corrected according to the following rule:

For each inch (25 mm.) below 29.92 inches (760 mm.) barometric reading add 1.6° F. to the flash point, and for each inch above subtract 1.6° F.

Viscosity (30.4).*—Determine the viscosity of fuel oils on the Saybolt furol viscosimeter at 122° F. If the oil shows a viscosity of less than 25 seconds, Saybolt furol, at 122° F., determine the viscosity with a universal Saybolt viscosimeter at the same temperature. For oils showing a viscosity of less than 32 seconds, Saybolt universal, at 122° F., determine the viscosity in the Saybolt universal viscosimeter at 100° F. Oils having a viscosity of less than 32 seconds, Saybolt universal, at 100° F. are not considered to be fuel oils.

The method of operation of the Saybolt furol viscosimeter is the same as that for the Saybolt universal viscosimeter as described on page 331. Furol viscosity multiplied by 10 gives viscosity on the universal Saybolt at the same temperature.

Water and Sediment (by Centrifuge) (300.3).†—The method for determination of water and sediment by means of the centrifuge is widely used but it should be remembered that the amount of water obtained is nearly always lower than the actual water content and that the reading on the centrifuge tube includes both the sediment and the precipitated water. (For accurate determination of the water content see p. 247.) The centrifuge method should not be used on oils having a Furol viscosity greater than 100 at 122° F.

The difficulties in obtaining representative samples for this determination are unusually great and the importance of sam-

* *Am. Soc. Testing Materials,* Method D88-21T.

† *Am. Soc. Testing Materials,* Method D96-21T.

pling cannot be too strongly emphasized. The sample must be thoroughly representative of the material in question and the portion used for the test must be thoroughly representative of the sample itself.

Make the test on a centrifuge capable of whirling at the required speed at least two 100-cc. centrifuge tubes filled with water. The tube carriers should be so designed that the glass centrifuge tubes may be cushioned with water, rubber or other suitable material and the 2 holders should be surrounded during the operation by a suitable metal shield or case strong enough to eliminate danger if any breakage occurs. The preferred form of centrifuge should have a diameter of swing (tip to tip of whirling tubes) of 15–17 inches and a speed of at least 1500 r.p.m. or the equivalent. If the available centrifuge has a diameter of swing varying from these limits, it must be run at the proper speed to give the same centrifugal force at the tips of the tubes. The proper speed may be calculated from the following formula, in which d represents diameter of swing of the centrifuge used:

$$\text{r.p.m.} = 1500\sqrt{\frac{16}{d}}$$

The centrifuge tubes should be made of suitable glass and thoroughly annealed, of a total capacity of about 125 cc., with the mouth suitably constricted for closing with a cork. The graduations should be clear and distinct, reading upward from the bottom of the tube as follows:

Range, cc.	Scale of Divisions, cc.	Limit of Error, cc.	Numbered, cc.
0–3	0.1	0.05	1, 2, 3
3–5	0.5	0.2	4, 5
5–10	1.0	0.5	6, 8, 10
10–25	5.0	1.0	15, 20, 25
50–100	50.0	1.0	50, 100

The shape is optional, provided it does not conflict with other requirements. Satisfactory types are shown in Fig. 13.

A water or oil bath should be provided of sufficient depth for immersing the centrifuge tubes in a vertical position to the 100-cc. mark and capable of being heated to 100° F.

Procedure.—Measure exactly 50 cc. of 90% benzol into each of 2 centrifuge tubes and add to each exactly 50 cc. of the oil to be tested. Tightly stopper the tubes and shake vigorously until the contents are thoroughly mixed. Immerse the tubes in the bath at 100° F. up to the 100-cc. mark for 10 minutes, then place the tubes in the centrifuge on opposite sides and whirl at the rate of 1400–1500 r.p.m., or the equivalent, for 10 minutes. Read and record the combined volume of water and sediment at the bottom of each tube, estimating to 0.1 cc. if possible; then replace the tubes in the centrifuge again, whirl for 10 minutes, remove and read the volume of water and sediment as before. Repeat this operation until the combined volume of water and sediment in each tube remains constant for three consecutive readings. Usually not more than four whirlings will be required. Read the combined total volume of water and sediment on each tube and record the sum of the two readings as "percentage of water and sediment, centrifuge method."

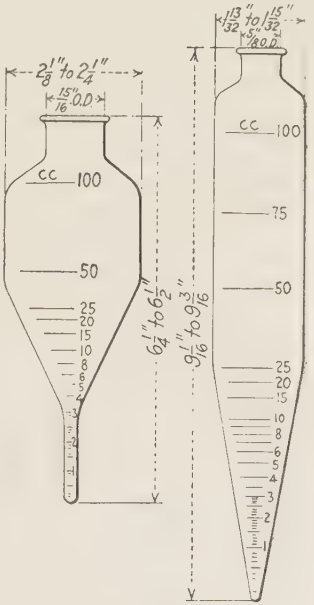


FIG. 13.—Centrifuge Tubes (A. S. T. M.)

With care and the proper attention to details duplicate determinations by this method should not differ by more than 0.2 cc., provided the centrifuge tubes are accurate and readable to this degree.

Water.*—The method in general is similar to the Xylol Method as described on page 358, except that instead of using Xylol for the diluent, water-free gasoline is used of the following specifications:

* Method 300.11 of the Federal Specification Board differs somewhat from the method here given, but is the same in principle.

When subjected to distillation by the A. S. T. M. method it should show 5% at a temperature not above 100° C. nor below 90° C., and 90% at a temperature not above 205° C.

Measure exactly 100 cc. of the oil in an accurate 100-cc. graduated cylinder at room temperature and pour into a 500-cc. distillation flask. Rinse out the graduated cylinder with two successive 50-cc. portions of the gasoline and transfer to the distillation flask, allowing the cylinder to drain each time. Mix the oil and gasoline in the distillation flask by swirling and introduce a boiling-stone, such as a small piece of unglazed porcelain, to prevent bumping. Insert the thermometer in the neck of the flask so that the top of the thermometer bulb is level with the bottom of the vapor outlet tube where the latter is joined to the neck of the flask. Distill the mixture at such a rate that 2–4 drops per second fall from the end of the condenser. Collect the distillate in a 100-cc. tube with the bottom constricted and graduated to 0.1 cc. A so-called Xylol funnel, or one of the centrifuge tubes described previously, may be used. Continue the distillation at the prescribed rate until the thermometer indicates a temperature of 400° F. and all condensed water has disappeared from the walls of the distillation flask and out of the condenser. The operation usually requires less than 1 hour. If a persistent ring of condensed water appears in the condenser tube, it may be removed by increasing the rate of distillation for a few minutes. Read and record the number of cc. of water in the bottom of the tube at room temperature.

With proper care and attention to details duplicate determinations of water by this method should not differ from each other more than 0.2 cc. provided the graduated receiver is accurate and readable to this degree.

Note.—When the sample contains more than 10% of water, use 50 cc. instead of 100 cc. and double the reading of the water.

Sediment (by Extraction) (300.2).—Dry for an hour at 105° C. an alundum porous thimble* 1 inch in diameter by 2.75 inches high, weighing between 15 and 17 grams. (If the thimble is a new one, extract it thoroughly with benzol before drying and

* The thimbles listed as 5163 R.A. 98 by the Norton Co., Worcester, Mass., are suitable.

weighing.) Place approximately 10 grams of the sample in the thimble and weigh to the nearest 0.01 gram. Place this in an extractor of the Underwriters' type (see p. 752). The thimble must be suspended directly from the condenser so that it is completely surrounded by the boiling solvent. Siphon extractors must not be used. Cover the bottom of the Erlenmeyer extraction flask with about 0.5 inch of 90% benzol and extract on the hot plate until the solvent dropping from the thimble is colorless. Dry the thimble for 1 hour at 105° C. and weigh accurately. Repeat the extraction until the weight of the dry thimble and sediment is constant.

NOTES.—(1) The rate of extraction shall be such that the mixture of oil and benzol in the thimble does not rise to within $\frac{1}{4}$ inch of the top.

(2) If the amount of mineral sediment is desired, ignite the thimble and contents in a muffle at a red heat until all carbon has burned off; cool in a desiccator and weigh.

Sulfur (520.21).*—Determine sulfur in the bomb calorimeter as described on page 252, using 0.6–0.8 gram of the oil. Duplicate determinations should agree within 2% of the total sulfur found.

Heating Value (B.t.u.).—Follow the procedure of the method described on page 250, correcting for the percentage of sulfur previously found.

NOTE.—There is considerable difference of opinion as to whether or not the B.t.u. determination on fuel oils should be corrected for the sulfur content. In a letter from the Bureau of Mines at Washington dated Apr. 15, 1924, we are advised that "The B.t.u. determinations as reported at the Pittsburgh Station, are corrected for sulfur the same as they are in coal analyses." All determinations made in our laboratory are corrected for sulfur unless otherwise instructed.

Carbon Residue (500.11).—This test is required by the Government on special fuel oils for Diesel engines in submarines. Follow the Conradson procedure described on page 339.

Precipitation Number (310.1).†—This test is also required by the Government on special fuel oils for Diesel engines in submarines. It is the number of cc. of precipitate formed when 10 cc. of the oil are mixed with 90 cc. of petroleum naphtha of definite quality

* *Am. Soc. Testing Materials*, Method D129-22T.

† *Am. Soc. Testing Materials*, Method D91-21T.

and centrifuged under definitely prescribed conditions. The petroleum naphtha shall have a sp. gr. at 60° F. of 0.695–0.705; an initial boiling point of 45–55° C.; and an end-point not higher than 120° C. The centrifuge and centrifuge tubes are the same as previously described under the test for Water and Sediment.

Place exactly 10.0 cc. of the oil in each of 2 clean dry centrifuge tubes at room temperature. Fill each tube to the 200-cc. mark with petroleum naphtha and close tightly with a softened cork. Invert each tube at least 20 times, letting the liquid drain thoroughly from the tapered tip of the tube each time; then place in a water bath at 90–95° F. for 5 minutes, removing the corks momentarily to relieve any pressure. Again invert each tube at least 20 times exactly as before. The success of the method depends to a large degree upon having a thoroughly homogeneous mixture which will drain quickly and completely from the tapered tip when the tube is inverted.

Place the two tubes in the centrifuge on opposite sides and whirl at a rate of 1400–1500 r.p.m., or equivalent, for 10 minutes. Read and record the volume of sediment at the bottom of each tube, estimating to 0.05 cc. if possible. Then place the tubes in the centrifuge and again whirl for 10 minutes as before. Repeat the operation until the volume of sediment in each tube remains constant for three consecutive readings. Usually not more than four whirlings are required.

Read the volume of the solid sediment at the bottom of each tube, estimating to 0.1 cc. or closer. If the readings differ by not more than 0.1 cc., report the average as "A. S. T. M. Precipitation Number." If the readings differ by more than 0.1 cc., make two more determinations and report the average of the four.

HEATING VALUE AND SULFUR CONTENT OF LIQUID FUELS

General.—This method is to be employed for determining the B.t.u. and sulfur content of such liquids as oils, coal tar products, gasoline, alcohol, etc.

Heating Value—British Thermal Units.—Calorimetric determinations are made in an Emerson bomb calorimeter with a gold lining.

Weigh the liquid directly in a dried, weighed, No. 00 gelatin capsule (Parke, Davis & Co.). In order to avoid incomplete

combustion from scattering of material with explosive violence, it is absolutely requisite that the capsule be very carefully filled so that no air bubbles are enclosed. To insure this shake the liquid well and pour a little into a small open dish. Fill each half of the previously weighed capsule, and while still immersed fit the halves of the capsule tightly together. Then remove the capsule, dry it thoroughly, weigh immediately and place in the fuel tray, which is lined with recently ignited asbestos. Coil the iron wire around the capsule. Place about 10 cc. of water in the bottom of the bomb. Screw the lid tightly down on the lead gasket and force oxygen slowly into the bomb. When testing liquids of the nature of alcohol, employ a pressure of 18–20 atmospheres (270–300 pounds per square inch); for those similar to gasoline, use a pressure of 25 atmospheres (375 pounds); and for materials like fuel oil or lubricating oil, use a pressure of 30 atmospheres (450 pounds).

The bomb is placed in the bucket which contains 1900 grams of water at a temperature of approximately 5–5.5° C. lower than the room temperature. The actual determination is completed exactly as for Coal (p. 219).

Calculation.—Calculate the result as described on page 221. The result thus obtained is further corrected as follows:

Deduct from the total B.t.u. generated the weight of the capsule multiplied by its heating value in B.t.u. This result, divided by the weight of the liquid taken, gives the B.t.u. per pound of the sample.

Notes.—(1) To calculate B.t.u. per gallon determine the sp. gr. of the liquid at 15.5° C. and multiply this by $8\frac{1}{3}$* and then by the B.t.u. per pound.

(2) In case it is found that the calorimetric value of the liquid cannot be determined with the liquid alone, recently ignited asbestos may be used as an absorbent. This method is resorted to when the liquid explodes violently and the determination is incomplete, as is shown by carbonaceous residues in the bomb. Ignite the asbestos in a hot muffle for 4 hours to insure the removal of any combustible matter. Weigh the capsule alone, fill with the ignited asbestos, and weigh again. Then fill the capsule with the liquid by means of a small pipette and weigh again to obtain the weight of the liquid taken.

(3) *Heating Value of Capsules.*—The capsules after being dried should be kept in a rubber-stoppered bottle. The calorific value of the dried capsules

* One gallon of pure water at 15.5° C. weighs 8.3335 pounds.

per gram is obtained by weighing 5 capsules and burning them together in the bomb. The average result of check determinations thus run is taken as the heating value per gram of the capsules. The heating value of the capsule used, expressed in B.t.u., is deducted from the total number of B.t.u. developed in the bomb.

Sulfur.—The method of determining the sulfur content of liquids from the bomb washings after combustion in the bomb is accurate, practicable and rapid, and is recommended in preference to all other methods.

The pressures given above under B.t.u. determinations are higher than is required for the calorific determination alone but by using these amounts it has been found that the C and S are completely burned.

After the regular calorimetric determination has been made, as outlined above, cool down the bomb to tap-water temperature. Then open and wash the contents into a beaker and titrate as usual. Add 5 cc. of a saturated solution of Na_2CO_3, heat to boiling for 10 minutes and then filter and wash 6 times with hot water. To the filtrate add 10 cc. of saturated bromine water, make slightly acid with HCl and boil to expel liberated Br and CO_2. Add slowly from a pipette 10 cc. of a 10% solution of $BaCl_2 \cdot 2H_2O$. Continue the boiling for 15 minutes and let stand overnight just below the boiling point. Complete the sulfur determination as described under Sulfur in Coal (p. 215). Run a blank sulfur determination on one of the capsules. Calculate the percentage of sulfur from the weight of $BaSO_4$, after deducting the blank.

CALCULATION.—$BaSO_4 \times 0.1373 = S$.

REFERENCES.—Strong and Stone: *Bur. Mines Bull.* 43, "Comparative Fuel Values of Gasoline and Denatured Alcohol in Internal Combustion Engines." (1912).

Allen and Robertson: *Bur. Mines Tech. Paper* 26, "Methods of Determining the Sulfur Content of Fuels, Especially Petroleum Products," (1912).

CHAPTER VI

ANALYSIS OF PAINTS AND PAINT MATERIALS

TURPENTINE

General.—The nature of a turpentine and whether or not it is adulterated can best be determined by careful distillation and examination of the various fractions as to sp. gr., index of refraction and boiling point.

Procedure.—Weigh 500 grams of the turpentine into a round-bottom flask of about 1-liter capacity. Connect the flask by means of a tightly fitting stopper to a Hempel column of the exact dimensions shown in Fig. 14. In the top of the Hempel column place a thermometer with the bulb reaching to within 1 inch of the glass beads, and connect the side-arm to a condenser. Drop into the flask a small flat coil of copper or nickel wire to prevent bumping and place the flask and contents on a sand bath. If the room temperature is very low, it may be necessary to place a shield of asbestos board around the column. Distill the turpentine at a maximum rate of 2 drops per second. It is important that this rate shall not be exceeded. Collect the distillate in weighed flasks or cylinders of about 100-cc. capacity. While the temperature of distillation is changing rapidly the fractions collected should be small, varying from 4–5%, and when

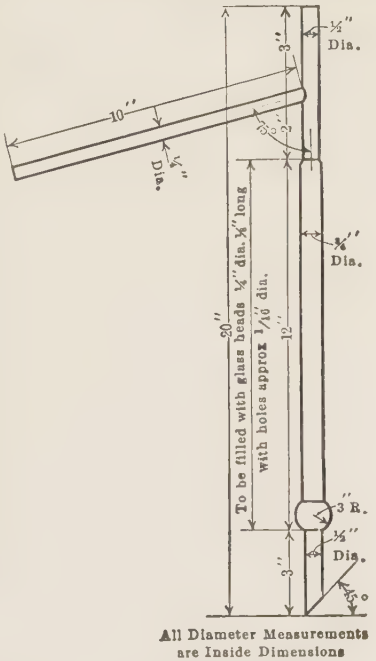


FIG. 14.—Hempel Column.

the temperature is slow and regular they may be increased to 10–12%. Usually it is unnecessary to continue the distillation after a temperature of 180° C. (corrected) has been reached, unless there is a large amount of residue at this stage.

As soon as a fraction has been collected, immediately stopper the flask or cylinder in which it is contained. Take the weight of each fraction and record the temperature at which the first drop of the fraction distilled. Also determine the sp. gr. at 15° C. and index of refraction at 15° C. of each fraction.

Boiling Point.—Correct the boiling temperature as actually read on the thermometer:

(1) For the prevailing barometric pressure, by adding 0.056° for every mm. which the barometer reads below 760 mm. and subtracting a corresponding amount for every mm. above 760 mm.

(2) For the emergent stem of the thermometer, according to the following formula:

$$\text{B. P.} = \text{T} + 0.000143\ (\text{T} - t)\ \text{N},$$

where B. P. is the corrected boiling point sought, T is the observed temperature, t is the mean temperature of the thermometer stem above the cork (measured by fastening by means of rubber bands to the thermometer in the Hempel column another thermometer with its bulb at the middle of the exposed thread of mercury), and N is the length, expressed in degrees, of the mercury column above the cork.

Specific Gravity.—Determine the sp. gr. by means of a Westphal balance, making the determinations at room temperature and correcting to 15° C. by using the factor 0.00083 for every degree C. of difference from this standard temperature. This correction is to be added for temperatures above 15° C. and to be subtracted for temperatures below 15° C. For small fractions the sp. gr. may be taken with the Westphal balance by placing the liquid in a test-tube supported in a flat cork. Since the correction for temperature is large, take special care to make the temperature readings accurate when the gravity is determined.

Index of Refraction.—Determine the index of refraction by means of the Abbé refractometer, taking the readings at room temperature and correcting by adding to the observed index

0.00047 for every degree above the standard temperature of 15° C., and subtracting for temperatures below.

Recording Results.—Plot the 3 curves for corrected boiling point, specific gravity and refractive index, respectively, on the same sheet of paper, plotting the percentage (by weight) of each fraction vertically and the other factor horizontally.

Interpretation of Results.—The typical curves of pure gum and wood turpentine are shown in Fig.15. An unadulterated sample will show curves which may be slightly misplaced to the right or

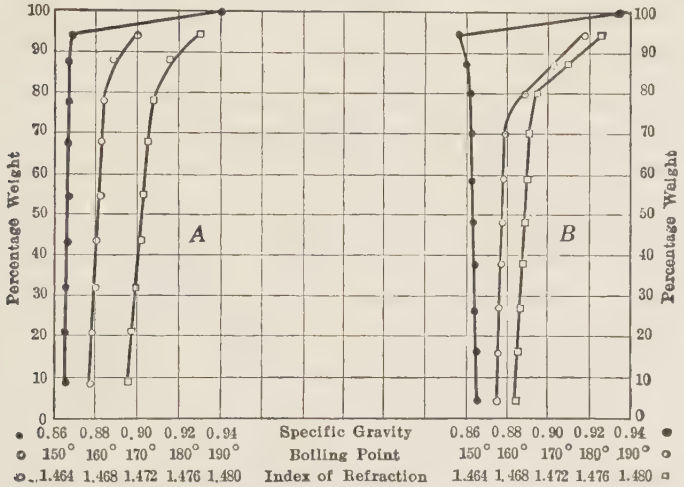


FIG. 15.—Typical Curves Showing Specific Gravities, Boiling Points and Indices of Refraction of: *A*. Pure Gum Turpentine. *B*. Wood Turpentine.

left but will be parallel to these curves. In general, for a pure gum turpentine the first fraction of the distillation should give figures within the following limits:

Refractive index at 15° C.....	1.4700–1.4725
Sp. gr. at 15° C.....	0.864–0.866
Corrected boiling point.....	156–157.5° C.

Pure gum turpentines of which the first fraction falls outside these limits are rare, but if the rest of the curve is normal such a turpentine probably is not adulterated.

REFERENCE.—*U. S. Dept. Agr., Forest Service Bull.* 105.

TURPENTINE

Electric Railway Specifications

General.—The material desired is pure gum or refined steam-distilled turpentine, free from adulteration.

Requirements.—Turpentine must meet the following requirements:

1. *Appearance.*—Clear and practically water-white.

2. *Specific Gravity.*—Sp. gr. at 15.5° C. not less than 0.862 nor more than 0.872.

3. *Distillation.*—When 200 cc. are distilled as below described, 95% should pass over below 170° C.

Conduct the distillation in a 300-cc. flask 8 cm. in diameter with the side tube 8 cm. from the main bulb and the neck extending 8 cm. above the side tube. The diameter of the neck is 2 cm.; of the side tube, 5 mm. Fit into the stopper in the neck a thermometer (reading from 145–200° C.) with the bulb opposite the side tube of the flask and the 175° C. mark below the stopper. Conduct the distillation so that about 2 drops of distillate come over per second.

4. *Residue on Evaporation.*—When 10 cc. of the sample are placed in a glass crystallizing dish 2.5 inches in diameter and $1\frac{1}{8}$ inches high and evaporated on the open steam bath with a full head of steam for 3 hours, the amount of residue shall not weigh over 0.15 gram. One drop allowed to fall on a clean white paper must completely evaporate at room temperature (20° C.) without leaving any stain.

5. *Polymerization Test.*—When 5 cc. of the sample are treated with conc. H_2SO_4 according to the following method, not over 0.50 cc. shall remain undissolved at the end of 30 minutes. The unpolymerized residue shall be viscous in nature and show a refractive index between 1.50 and 1.52 at 15.5° C.

Method.—Add slowly 5 cc. of turpentine to 25 cc. of conc. H_2SO_4 in an ordinary graduated, narrow neck, Babcock milk bottle (the smallest divisions on the neck of these bottles are 0.04 cc.); shake the flask with a rotary motion to insure gradual mixing, keeping cool, if necessary, in ice water and not allowing the temperature to rise above 60–65° C. Agitate thoroughly and maintain at about 65° C. with frequent agitation for 1 hour.

Cool and fill the flask with conc. H_2SO_4, bringing the unpolymerized residue into the graduated neck. Let stand 0.5 hour and read the volume of unpolymerized residue. Note its consistency and color and determine its refractive index at 15.5° C.

NOTE.—If the residue is water-white and limpid and does not show the proper refractive index, repolymerize with 38 N H_2SO_4 (100.92% H_2SO_4 by weight, prepared by mixing conc. H_2SO_4 with sufficient fuming H_2SO_4 to give this strength) as described by Veitch in *U. S. Dept. Agr., Bur. Chem., Bull.* 135, 50 (or *Circ.* 85).

LINSEED OIL

General.—Raw linseed oil is the refined oil obtained from flaxseed or linseed, generally by hydraulic pressing. For use in paint, etc., to obtain quicker drying qualities, raw oil may be heated with very small amounts of certain "driers" such as oxides of Pb, Mn, Co, etc. Oil thus prepared is called boiled linseed oil.

Oils from different countries vary somewhat in composition. Pure linseed oils from North America should show about the following "constants":

TABLE X—CONSTANTS OF NORTH AMERICAN LINSEED OIL

	Raw		Boiled	
	Maximum	Minimum	Maximum	Minimum
Sp. gr. at 15.5° C.	0.938	0.932	0.945	0.935
Refractive index at 25° C.	1.4805	1.4790	.....	.....
Saponification number	195	189	195	185
Iodine number	.....	180	.....	160
Unsaponifiable matter	1.50%	.....	1.50%	.....
Acid number	6.0	.....	10.0	.....
Drying test	75 hrs.	.....	24 hrs.	.....

A low iodine number accompanied by a high sp. gr. may indicate polymerization due to old age or excessive heating. High-grade oils should also be clear and free from "foots" or sediment.

Preparation of Sample.—See page 298.

Specific Gravity at 15.5° C.—See page 298.

Refractive Index at 25° C.—See page 299.

Saponification Number.—See page 309.

Iodine Number.—See page 310.

Unsaponifiable Matter.—See page 340.

Acid Number.—See page 311.

Drying Test.—Flow some of the sample over a piece of clean glass and let drain in a vertical position at about 20° C., testing at intervals for "tackiness" with the finger. Note how long it requires for the film to become dry.

TUNG OIL

General.—This oil is also known under various other names such as China Wood Oil, Japanese Wood Oil, Wood Oil, or Nut Oil. It has a strong characteristic odor. Most of it comes from China; a small amount comes from Japan.

Cold drawn oil is pale yellow and called White Tung Oil; hot pressed oil is dark brown and called Black Tung Oil. Very little of the latter comes to this country.

The constants of pure Chinese oil are as follows:

Sp. gr. at 15.5° C	0.939–0.943
Saponification number	190–200
Iodine number	150–166
Refractive index at 25° C	1.515–1.520
Heating test (Browne method)	max. 12 minutes
Iodine jelly test	max. 4 minutes

Japanese oil has a lower sp. gr. (about 0.933–0.935 at 15.5° C.)

For further properties, see Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," Vol. II.

Specific Gravity at 15.5° C.—See page 299.

Saponification Number.—See page 309.

Iodine Number.—Follow the method on page 310 with the following modifications: Weigh out between 0.10 and 0.20 gram and use an excess of 52–58% of Wijs solution. Let the absorption continue for 1 hour at 20–25° C.

Free Fatty Acids.—See page 311.

Refractive Index at 25° C.—See page 299.

Unsaponifiable Matter.—See page 340.

Heating Test (Browne Method).—Place in a $6 \times \frac{5}{8}$ inch test-tube 5 cc. of water and make a mark at the 5-cc. level. Then dry

the test-tube and insert a cork perforated so that a glass rod of 3 mm. diameter can move freely. Fill a copper dish about 5 inches high by 2.5 inches inside diameter with cottonseed oil to a height of 3 inches. Insert a thermometer so that the bulb is $\frac{5}{8}$ inch from the bottom of the dish.

The thermometer should be nitrogen-filled, total immersion, length 4–4.5 inches, graduated from 210–310° C. in 2° intervals; length between 210 and 310° C. not less than 2.5 inches. If preferred, a longer thermometer (12 inches, with graduations from 100–400° C.) may be used, in which case make corrections for the emergent stem. (See U. S. Bureau of Standards, Stem Correction Sheet No. 44.)

Heat the bath of cottonseed oil slowly to 293° C.; then place in it the tube containing 5 cc. of the oil sample, so that the bottom is level with the lowest part of the thermometer bulb. Note the time and remove the heat for about 45 seconds; then reapply the heat. Before 2 minutes have elapsed, the temperature of the bath will have fallen to 282° C. Hold at this point as steadily as possible. When the sample has been in the bath about 9 minutes, raise the glass rod at intervals of 0.5 minute and when the rod is firmly set, note the time. Remove the flask at once; heat the bath again to 293° C. and repeat the experiments with another portion of the sample.

No stirrer is necessary in the bath, but it should be protected with a screen. When the cottonseed oil bath becomes tarry and viscid, it should be renewed.

Pure tung oil should "set" within 12 minutes.

Iodine Jelly Test.—Weigh accurately 2.500 grams of the sample into a wide-necked 200-cc. Erlenmeyer flask; add 10 cc. of $CHCl_3$ from a pipette and stopper the flask immediately. Carefully insert into the flask a small glass vial so that it stands upright, and into this vial pipette 10 cc. of a solution of iodine in $CHCl_3$ containing 0.035–0.036 gram of iodine per cc. Place the flask in a bath containing water at 25–26° C. and let stand a few minutes, keeping the flask stoppered except when necessary to remove it.

Tilt the flask and rotate so that the vial is upset and the contents are thoroughly mixed, starting a stop watch at the same time. Keep the flask in the bath at 25–26° C., and every 15 seconds tilt the flask toward a horizontal position. Note the

time required for formation of a jelly that does not flow but sticks to the bottom of the flask or slides in a mass. Record the time to the nearest quarter minute. Pure tung oil should require 2.75–3.25 minutes to jell.

If the temperature of the laboratory varies more than 2 or 3° C. from 25° C., place the flask containing the iodine solution in the bath and let it remain for several minutes before pipetting out the 10 cc. for test.

The $CHCl_3$ used to dissolve the oil and to prepare the iodine solution should conform to U. S. P. requirements and have a sp. gr. of 1.480–1.481 at 25° C. If the sp. gr. is too low, wash the $CHCl_3$ with water; if too high, add a little 95% grain alcohol.

The iodine solution is prepared as follows: Treat an excess of iodine with warm $CHCl_3$; shake for a few minutes; cool to about 20° C. and filter through glass wool. Pipette 10 cc. of the solution into an Erlenmeyer flask containing 10 cc. of 10% KI solution and titrate with 0.1 N thiosulfate. Calculate the iodine content and dilute with $CHCl_3$ so as to obtain an iodine content of 0.035–0.036 gram per cc. After dilution, titrate again to make sure the solution is of proper strength.

The above method is empirical and details must be followed exactly.

References.—Lewkowitsch. "Chemical Technology and Analysis of Oils, Fats and Waxes," **2**; *Am. Soc. Testing Materials*, Standard D12-16.

MIXED PAINTS AND PIGMENTS IN OIL

General.—Paints from the chemical point of view may be considered as consisting of two parts, (1) the vehicle, and (2) the pigment.

The vehicle may consist entirely of linseed oil, which is usually the case with individual paste pigments. Frequently, however, especially in the case of mixed paints, it also contains a certain amount of driers and of thinner (either turpentine or mineral spirits); and in the case of enamels and high-gloss paints, the vehicle may also contain varnish or varnish gums.

The pigment may be a simple chemical compound, such as ZnO, or a mixture of several substances. Zinc oxide, basic carbonate white lead, and basic sulfate white lead, are among the most important ingredients of paint pigments. Red lead, blue

lead and graphite are largely used as protective coatings for iron and steel. Numerous other substances are also used as paint pigments, many of which are by no means simple chemical compounds, such as mineral silicates, yellow ochre, umber, lithopone, etc.

The most important paint pigments are the following:

WHITE PIGMENTS.—1. *Basic Carbonate White Lead* (*Corroded White Lead*) is approximately $2PbCO_3 \cdot Pb(OH)_2$.

2. *Basic Sulfate White Lead* (*Sublimed White Lead*) is largely basic lead sulfate, usually containing a little ZnO. A typical analysis would show: $PbSO_4$ 76.8%, PbO 17.3%, ZnO 5.6%.

3. *Zinc Oxide* (*Zinc White*), ZnO.

4. *Lithopone* is made by simultaneous precipitation of ZnS and $BaSO_4$ and generally contains about 70% of the latter.

5. *Barytes* (*Blanc Fixe*) is $BaSO_4$.

6. *Silica* (*Silex*). This may be ground silica or diatomaceous (infusorial) earth.

7. *Asbestine* is essentially a silicate of Mg and is made by grinding waste asbestos.

8. *Clay* (*Kaolin*) is a hydrated aluminum silicate.

9. *Gypsum* (*Terra Alba*) is $CaSO_4 \cdot 2H_2O$. Anhydrous $CaSO_4$, or *Burnt Gypsum*, is used as an extender in Venetian Red.

10. *Chalk*, *Paris White*, *Whiting*, *Alba Whiting*, etc. These are all $CaCO_3$ but differ somewhat in their physical conditions.

BLACK PIGMENTS.—1. *Lampblack* is a grayish black, bulky pigment. It is the soot produced by burning oils, resins, etc.

2. *Gas Black* (*Carbon Black*) is made from natural gas. It is much blacker than lampblack.

3. *Bone Black* is made by carbonizing bones. It contains 10–20% carbon, the remainder being largely calcium phosphate.

4. *Ivory Black* (*Drop Black*) is a high-grade bone black made from ivory waste.

NOTE.—The color of bone black and ivory black may be modified by the addition of Prussian blue.

5. *Charcoal Black* is produced from vegetable charcoal.

6. *Graphite* (*Plumbago*) is a form of carbon occurring as a natural mineral. That used in paints may run up to 85% carbon, the remainder being silicious matter.

Red Pigments.—1. *Indian Red* is essentially Fe_2O_3—dark purplish red.

2. *Tuscan Red* is Indian red enriched by an alizarin lake, giving a crimson shade. It is often toned down with $BaSO_4$, $CaCO_3$, or gypsum.

3. *Venetian Red* is also largely Fe_2O_3, but is brick red in color and contains more or less gypsum (or, in inferior grades, $CaCO_3$ or $BaSO_4$).

4. *Red Lead* is a brilliant scarlet but is used as a protective coating and not as a tinting pigment. When chemically pure it is Pb_3O_4 but the commercial product contains 70–99% Pb_3O_4 (usually over 85%), the remainder being PbO incidental to manufacture, unless the material is intentionally adulterated.

5. *Orange Mineral* is a form of red lead with a lower sp. gr. and lighter color than the usual form.

6. *English Vermilion* is HgS. It is not much used now because of its high price.

7. *American Vermilion* (*Chrome Red, Scarlet Lead Chromate*) is a basic chromate of lead.

8. *Lakes* are formed by combining the coloring matter of certain dyes with inorganic carriers, such as $BaSO_4$, $CaCO_3$ or clay. They are generally used in paints with a large amount of other pigment for brightening or modifying the color. Among the most important lakes are the vermilions and scarlets made from para-red, and from alizarin. The dye (color) may be as little as 5% in the lake itself.

Yellow Pigments.—1. *Chrome Yellows* are chromates of lead of varying color and composition.

(*a*) *Chrome Yellow Light* (*Chrome Yellow Lemon or Canary*) contains more or less $PbSO_4$ or other insoluble Pb compound intimately mixed with $PbCrO_4$.

(*b*) *Chrome Yellow Medium* is pure $PbCrO_4$.

(*c*) *Chrome Yellow Orange* (*Chrome Orange*) is a basic lead chromate which may vary in color from pale orange to nearly scarlet.

2. *Ochers* (*Yellow Ochers*) are natural earths whose color is due to hydrated iron oxide (limonite, $2Fe(OH)_3 \cdot Fe_2O_3$) and varies from citron yellow to almost olive. The hydrated iron oxide may vary from 10–60%, the remainder being silicious

matter or clay. *Golden Ocher* is yellow ocher modified with $PbCrO_4$.

3. *Raw Siennas* resemble ochers in general composition, but are brownish yellow and generally contain a little manganese.

Brown Pigments.—1. *Burnt Sienna* is made by calcining raw sienna, which changes the color to an orange red or red brown.

2. *Raw Umber* is a natural earth pigment of yellow-brown color inclining toward the olive and is similar in composition to sienna but contains considerable manganese oxide.

3. *Burnt Umber*, made by calcining raw umber, has a rich brown color, darker than the raw but free from red.

4. *Vandyke Brown* (*Cassel Earth, Cologne Earth*) is a natural pigment of a carbonaceous nature and is distinguished by its solubility in dil. alkali.

Blue Pigments.—1. *Prussian Blue* is made by precipitating a soluble ferrocyanide with $FeSO_4$ and oxidizing the precipitate. If the precipitate were pure and completely oxidized it would, of course, have the composition $Fe_4[Fe(CN)_6]_3$. The commercial product, however, varies considerably in composition. *Chinese Blue* is a modification of Prussian Blue.

2. *Ultramarine* was formerly obtained from the semi-precious mineral lapis lazuli. It is now made artificially, however, and is quite cheap. It is essentially a double silicate of Al and Na with some sulfides or sulfates. It yields H_2S when treated with HCl and loses its color even with weak acids.

3. *Cobalt Blue* consists of oxides of Al and Co. Genuine cobalt blue is quite expensive and it is frequently substituted by ultramarine mixed with a little ZnO.

4. *Sublimed Blue Lead* consists mainly of $PbSO_4$ and PbO with smaller amounts of PbS, $PbSO_3$ and ZnO, with occasional traces of carbon. Its color is a dull steel gray and its principal use is as an inhibitive pigment for the prevention of corrosion of iron and steel. A typical analysis shows:

	Per cent
$PbSO_4$	49.8
PbO	37.7
PbS	6.1
$PbSO_3$	2.8
ZnO	1.0
Undetermined	2.6

Green Pigments.—1. *Chrome Green* is an intimate mixture of Prussian blue and chrome yellow and in this form is sold as "chemically pure." It is also put out as "commercial chrome green" which generally contains about 25% of the pure color and 75% of $BaSO_4$ or a silicate.

2. *Chrome Oxide Green* is Cr_2O_3, often more or less hydrated. It is an expensive pigment.

Analysis

It is impossible to outline a general method which will be applicable to all paints. The following procedures for the separation and determination of the amount of vehicle and pigment, however, are applicable to most paints and to pigments ground in oil.

Total Vehicle.—The vehicle may be separated from the pigment either by continuous extraction or by dilution with a suitable solvent and whizzing in a centrifuge.

By Continuous Extraction.—Mix the sample very thoroughly (see note 1 below), taking particular pains to stir up any pigment which has settled. Partly fill a small beaker with the well-mixed paint and place in it a stirring rod. Insert a plug of cotton in a Soxhlet extraction thimble (of double thickness if the paint contains ZnO or other extremely fine pigments), dry at 100° C. and weigh. Stand the thimble in another small beaker, and remove the cotton. Weigh the beaker with the paint, then fill the thimble about three-quarters full, pouring the paint carefully down the stirring rod. Again weigh the beaker with the stirring rod and determine the amount of paint which has been transferred to the thimble. Plug the thimble lightly with the cotton, place it in a Soxhlet extractor, fill the extractor nearly full of ether and let the paint and the thimble soak in it for at least 1 hour before starting the siphoning. Continue the extraction until the ether extract comes over colorless. Then remove the thimble, let the pigment dry, grind it to break up lumps, return to the thimble and again extract for at least 4 hours (or overnight). Finally evaporate the ether from the extract and dry to constant weight at 105–110° C. Also dry the thimble with the pigment at about 105° C. and weigh it. The difference between 100% and the sum of the percentages of the pigment and of the ether extract is a

rough indication of the amount of volatile thinner. In case only the total pigment and total vehicle are desired, the weight of the dried pigment and not of the extract should be used in making the calculations.

By Centrifuging.—Weigh two empty cylinders (4-ounce oil sample bottles are convenient), fill each about one-fourth to one-third full of the mixed paint, and again weigh. Add an equal volume of ether, mix thoroughly, place the cylinders in a centrifuge opposite each other, so that they counterbalance, and whiz until the pigment settles clear. Pour off or siphon off as much as possible of the clear liquid, refill the cylinders with ether, stir up the pigment and again centrifuge. Repeat the process until the pigment is free from oil. Remove the ether with a gentle air blast and dry the pigment to constant weight at 105° C.

Notes.—(1) If the sample is a large one, received in the original can, weigh the can as a whole, without shaking, remove as much of the clear vehicle as possible, and transfer it to a cork-stoppered flask or bottle. Weigh the can to obtain the amount of vehicle removed. Then mix thoroughly the contents of the can and transfer to another container. Clean out the empty can and weigh it. From these figures the analytical results can be calculated back to the original material.

(2) The method of centrifuging is more rapid than the continuous extraction method and in the case of very fine pigment which cannot be held by the thimbles it is preferable.

(3) In many cases it is preferable to use several solvents in sequence as follows: Extract with gasoline by means of the centrifuge, again extract with gasoline, then with benzene, and finally with ether, removing each time as much as possible of the clear extract. In the case of certain enamel paints, it is advisable to follow the gasoline treatment by a treatment with turpentine and then remove the turpentine with gasoline before treatment with benzene and ether.

(4) In the case of paints which settle with difficulty, better results are sometimes obtained by a mixture of solvents, such as a mixture of 6 parts of benzene and 4 parts of wood alcohol by volume.

(5) No extraction process will remove the last traces of the vehicle. The insoluble portion is probably oxidized linseed oil or metallic soaps.

Pigment.—Grind the dried pigment finely and make a qualitative analysis on a portion of it before attempting a quantitative analysis. The general procedure for a quantitative analysis of a mixed pigment is indicated on page 267, but the procedure may have to be considerably varied in individual cases. (See also methods for White Lead, Chrome Yellow, and Red Lead.)

Vehicle.—If the amount and condition of the sample will permit, make the analysis on the clear vehicle poured off from the original sample.

Thinner.—Weigh 50–100 grams of the separated vehicle (or a correspondingly greater amount of the original paint) into a 500-cc. flask connected with a spray trap and a vertical condenser and distill with steam.* Heat the flask in an oil bath nearly to 100° C. before passing in the steam and then raise the temperature to 130° C. Collect the distillate in 100-cc. graduated glass-stoppered cylinders which have previously been weighed. When the distillate comes over clear, or at least 300 cc. of water have been collected, stopper the cylinders and weigh them. Read the volume of water and of thinner, subtract the weight of water (1 cc. of water = 1 gram) and calculate the percentage of thinner, both by volume and by weight in the vehicle, and by weight in the original paint.

Instead of collecting the distillate in graduated cylinders, the entire distillate may be collected in a small weighed separatory funnel. Then let the layers separate sharply, draw off the water and weigh the funnel containing the thinner.

Determine the sp. gr. of the thinner at 15.5° C. and make a polymerization test and such other tests as will establish whether it is pure turpentine or a mixture of turpentine with mineral spirits (see pp. 253 and 256).

Analysis of Oil.—*Specific Gravity.*—Determine the sp. gr. at 15.5° C. of the original vehicle with a hydrometer or Westphal balance and correct for the amount of thinner and its sp. gr. as above determined.

Ash and Driers.—Determine the amount of ash in a porcelain crucible and its nature. If much Pb is present, part of it is lost in igniting to ash, and a quantitative analysis of the ash is therefore not accurate. For the quantative determination of driers see page 288.

Iodine Number.—Determine the iodine number of the oil freed from water after the steam distillation, bearing in mind that the constants of linseed oil which has been mixed with pigment,

* If alcohol, acetone, or other water-soluble solvent is present, it is necessary in order to determine these to run an additional distillation without steam.

especially Pb compounds, may be much altered and that an iodine number even as low as 100 is not an indication of the presence of other fatty oils. (See p. 310.)

Mineral Oil.—Determine the saponification number as described on page 309, and if the oil is not completely saponifiable, determine the amount of unsaponifiable oil. (See p. 340.)

Water.—Some specifications place a maximum limit on the permissible amount of water. The latter may be determined on the mixed paint by the Xylol Method, as described on page 358, using about 100 grams of the sample.

REFERENCES.—Holley and Ladd: "Mixed Paints, Color Pigments and Varnishes"; *U. S. Dept. of Agr., Bur. of Chem., Bull.* 109, revised; *Bur. Standards, Circ.* 69.

GREEN GRAPHITE POLE PAINT

General.—This method covers the analysis of Green Graphite Pole Paint delivered under specifications requiring a paint containing between 40 and 45% of pigment; the pigment to consist of amorphous graphite, silica, iron oxide and alumina, and tinting color, the latter composed of Prussian blue and chrome yellow.

NOTE.—Chrome yellows and chrome greens are sometimes toned down with $PbSO_4$ and barytes ($BaSO_4$). Small amounts of these substances, therefore, would not be cause for rejection.

Pigment and Vehicle.—Determine the proportions of pigment and vehicle by extracting a weighed quantity of the paint with ether or with low-boiling gasoline, either in a Soxhlet extractor* or with a centrifuge. Weigh the dry pigment.

Total Insoluble Matter.—Boil 1 gram of the dry pigment in a 250-cc. beaker with 30 cc. of conc. HCl for about 30 minutes. Add from time to time a drop of alcohol. Then add 50 cc. of water and boil again for 15 minutes. Filter on a filter paper which has been dried and weighed in a weighing bottle. Wash the residue thoroughly with hot water; dry in the weighing bottle, cool in a desiccator, and weigh.

Carbon.—Ignite the above residue in a platinum crucible until all C is burned off, cool in a desiccator and weigh. Report the loss as carbon.

* If an extractor is used, extract until siphonings are colorless, remove the pigment, dry, grind, and re-extract for at least 4 hours.

Barium Sulfate.—Moisten the residue in the crucible with a little water and add a few drops of dil. H_2SO_4. Then fill the crucible $\frac{2}{3}$ full of HF. Evaporate this off on a hot plate and repeat the operation to insure removal of all SiO_2. Ignite the residue gently until all SO_3 has been driven off. Fuse this residue (consisting of Fe_2O_3, Al_2O_3 and $BaSO_4$) with a considerable excess of $KHSO_4$, using a very low flame to avoid sputtering. Digest the fusion in water containing a little HCl. If completely soluble, no $BaSO_4$ is present. If there is any residue, filter, wash with hot water, ignite in a platinum crucible, and weigh as $BaSO_4$.

NOTES.—(1) The presence of $BaSO_4$ should be confirmed by fusing this residue with Na_2CO_3, boiling with water and filtering. Test the filtrate for SO_4; dissolve the residue in HCl and test for Ba.

(2) Save the filtrate from the $KHSO_4$ fusion for determination of insoluble iron and alumina.

Total Lead.—To the filtrate from the total insoluble, add NH_4OH until a precipitate begins to form and then just enough HCl to redissolve it. Dilute to about 500 cc.; saturate with H_2S, heat to boiling, let settle, and filter off the black PbS. Wash with H_2S water; then dissolve in conc. HNO_3, containing a little Br water. Filter out any sulfur, boil off bromine, dilute to about 200 cc., and make faintly alkaline with NH_4OH. Then add a slight excess of acetic acid. To the boiling solution add an excess of $K_2Cr_2O_7$ solution. Boil for 2 or 3 minutes until the precipitate settles clear. Filter on a weighed Gooch crucible, wash with hot water, dry at 100° C., set the Gooch crucible in a larger platinum crucible, ignite gently, cool in a desiccator and weigh as $PbCrO_4$.

NOTE.—Pb may be also determined as $PbSO_4$ as described under Total Lead in Chrome Yellow (p. 276).

Lead Chromate.—Boil the filtrate from the PbS until it contains no more H_2S, then add a few drops of HNO_3 and boil again. Precipitate the hydroxides of Fe, Cr, and Al with a slight excess of NH_4OH. Filter and wash with hot water. Dissolve in HCl and make up to 250 cc. Pipette 100 cc. of this solution (equivalent to 0.4 gram of the original pigment) into a beaker, add a slight excess of NH_4OH, cool and add about 1 gram of Na_2O_2, keeping the beaker covered with a watch glass. Digest on

the steam bath until evolution of gas has ceased; filter and wash with hot water. Redissolve the precipitate in HCl and reprecipitate with NH_4OH; and again add Na_2O_2, keeping the volume of solution small. Filter and wash. Combine both filtrates, make slightly acid with acetic acid and boil until all peroxide has been decomposed. Continue the determination as described under Lead Chromate in Chrome Yellow, using either the gravimetric or the volumetric method (see p. 277).

Iron Oxide and Alumina.—Insoluble Fe_2O_3 and Al_2O_3 are determined in the solution of the $KHSO_4$ fusion, after filtering out any $BaSO_4$ or undecomposed silica. To this filtrate add a few drops of HNO_3, heat to boiling and then add a slight excess of NH_4OH and boil until the odor of the latter is nearly gone. Filter, wash with hot water, ignite strongly and weigh as $Fe_2O_3+Al_2O_3$.

Soluble Fe_2O_3 and Al_2O_3 are determined on an aliquot of the filtrate from the PbS. Pipette 100 cc. (equivalent to 0.4 gram of the original pigment) into a beaker, add a few drops of HNO_3 and heat to boiling; precipitate with a slight excess of NH_4OH; filter, wash with hot water, ignite over a blast lamp and weigh. The residue consists of $Fe_2O_3+Al_2O_3+Cr_2O_3$. Subtract from this the Cr_2O_3 equivalent to the $PbCrO_4$ found. Add the difference to the insoluble iron oxide and alumina and report as Total Iron Oxide and Alumina.

Calculation.—$PbCrO_4 \times 0.2352 = Cr_2O_3$.

Silica.—SiO_2 is obtained by calculation as follows: The residue in the crucible after burning off carbon consists of SiO_2+BaSO_4 (if present)+insoluble Fe_2O_3 and Al_2O_3. From its weight, therefore, subtract the amount of the other substances as determined above and report the difference as Silica.

Prussian Blue.—Weigh 2 grams of the dry pigment into a Kjeldahl flask, and add 10 grams of anhydrous K_2SO_4 or Na_2SO_4 (free from N) and 30 cc. of conc. H_2SO_4. Heat over a Tirrill burner, gently at first, and then to copious fumes for 6–8 hours. Cool, dilute to about 250 cc. and add a few grains of granulated Zn and about 80 cc. of conc. NaOH solution.* Distill into 50 cc.

* Sufficient NaOH solution must be added to give a strong alkaline reaction after distillation is completed. See under determination of Nitrogen (p. 88).

of 0.1 N HCl until at least 100 cc. have come over. Titrate the excess of acid with 0.1 N alkali. Calculate the acid consumed to Prussian blue, $Fe_4[Fe(CN)_6]_3$.

CALCULATION.—1 cc. 0.1 N acid = 0.004772 gram Prussian blue.

NOTES.—(1) Any excess of Pb beyond that required for lead chromate should be calculated to lead sulfate.

$$PbCrO_4 \times 0.9383 = PbSO_4.$$

(2) Commercial Prussian blues seldom if ever conform strictly to the formula $Fe_4[Fe(CN)_6]_3$, but it is necessary to assume some formula in making the chemical calculation and the theoretical formula is the one usually taken.

RED LEAD AND ORANGE MINERAL

General.—Red lead and orange mineral in the pure state are oxides of lead (approximately Pb_3O_4), being probably mixtures of compounds of varying proportions of PbO and PbO_2. The commercial dry pigment is obtained in two grades, known as 85% and 95%, respectively.

Red Lead (Pb_3O_4).—Weigh accurately 1 gram of the sample into a 200-cc. Erlenmeyer flask, add a few drops of water and rub to a smooth paste with a flattened glass rod. Mix in a small beaker 30 grams of pure crystallized sodium acetate, 2.4 grams of KI, 10 cc. of water and 10 cc. of 50% acetic acid. Stir until all is liquid, warm gently and if necessary add 2–3 cc. more water. Cool to room temperature and pour into the flask containing the red lead. Rub with the glass rod until nearly all the red lead has been dissolved. Add 30 cc. of water containing 5–6 grams of sodium acetate and titrate at once with 0.1 N thiosulfate solution, adding the latter rather slowly and keeping the liquid constantly in motion by whirling the flask. When the solution has become light yellow, rub up any undissolved particles with the rod until free iodine no longer forms. Wash off the rod and add more thiosulfate solution until pale yellow. Finally add starch solution and titrate until colorless and then come back with 0.1 N iodine solution until the blue color is just restored. Subtract the iodine reading from the thiosulfate reading and calculate the difference to red lead.

CALCULATION.—1 cc. 0.1 N thio = 0.03428 gram Pb_3O_4.

For purposes of calculation it may also be assumed that 1 cc. 0.1 N thio = 0.03348 gram PbO. This, however, is really the equivalent of the Pb_3O_4 in terms of PbO.

Litharge.—Treat 1 gram with 20 cc. of conc. HCl. Cover and heat on the steam bath for 15 minutes. Add 100 cc. of hot water and boil. (If there are any insoluble impurities, filter them out and weigh.) Add NH_4OH until a white permanent precipitate forms. Redissolve with a slight excess of acetic acid. Heat to boiling, and precipitate with an excess of $K_2Cr_2O_7$ solution. Boil until the precipitate is granular and settles readily (2 or 3 minutes are generally sufficient), filter on a weighed Gooch crucible, wash with hot water, dry at 100° C., set the crucible inside a larger platinum crucible, ignite to dull redness and weigh as $PbCrO_4$. Calculate to PbO and subtract from the latter the equivalent of the Pb_3O_4, in terms of PbO. The difference will be the PbO actually present as such in the material.

CALCULATIONS.—$PbCrO_4 \times 0.6906 = PbO.$

$Pb_3O_4 \times 0.9767 = PbO.$

Water-soluble Matter.—Digest 10 grams of the sample with 200 cc. of hot water on the steam bath for 1 hour. Filter and wash with hot water until no residue is left on evaporating a few drops of the washings. Evaporate the filtrate to dryness in a weighed dish on the steam bath, heat for 30 minutes at 105–110° C., cool and weigh.

Fineness.—Dry a standard No. 200 brass or copper sieve in an oven at 105–110° C., cool, and weigh accurately. Weigh 50 grams of the pigment which has been previously thoroughly dried by heating in an oven at 105–110° C. Transfer to a wide-mouthed bottle or cylinder of about 300-cc. capacity, add about 200 cc. of dry kerosene, stopper, and shake vigorously for about 5 minutes. Remove the stopper, and, with a jet of kerosene, wash back into the cylinder any pigment adhering to the stopper. Pour about 50 cc. of the kerosene with the suspended pigment upon the sieve, let drain through, and gradually transfer the whole of the kerosene and pigment to the sieve, finally using a jet of kerosene to transfer the last of the pigment. With proper manipulation a large portion of the pigment will pass through the sieve during the process of transferring from the cylinder. When

all pigment has been thrown on the sieve, wash with a jet of kerosene until no more pigment passes through. To make sure that all particles have been thoroughly washed through, move the sieve from over the vessel, in which the main portion of kerosene and pigment has been caught, to over a clean glass dish resting on a white surface and wash all portions of the sieve with a jet of kerosene, using not less than 200 cc. of kerosene. The kerosene caught in this dish should be entirely free from pigment. If any pigment can be seen in the liquid, repeat the washing until at least 200 cc. can be washed through without showing any pigment. Then wash off with a jet of kerosene all pigment adhering to the frame of the sieve beneath the wire mesh. Finally, wash the kerosene from the sieve with petroleum ether, dry the sieve at 105–110° C., cool, and weigh. Report as percentage of Residue on 200-mesh Sieve. (The residue should be not more than 0.3% for a well-made material.)

If impracticable to weigh the sieve, wash the final residue by means of a jet of kerosene into a weighed Gooch crucible. Then wash out the kerosene with petroleum ether, dry and weigh the crucible with the residue.

Organic Coloring Matter.—Boil about 2 grams of the sample with 25 cc. of 95% ethyl alcohol, let settle and decant off the supernatant liquid. Boil the residue with water, decant as before and boil the residue with very dil. NH_4OH. If the alcohol, water or ammonia are colored, organic coloring matter is indicated, which is cause for rejection of the material. The quantitative determination of such coloring matter is very difficult and it is usually estimated "by difference."

Other Impurities.—The sample should be completely soluble in a mixture of HNO_3 and H_2O_2. If more than a faint cloud remains after this treatment, take a weighed sample and determine the percentage of this insoluble matter.

In case the sum of the percentages of Pb_3O_4, PbO, water-soluble matter and matter insoluble in HNO_3-H_2O_2 does not approximate 100%, other constituents are to be suspected and these may be tested for qualitatively and determined by the usual methods, looking particularly for nitrate, nitrite, carbonate and sulfate.

Reference.—*U. S. Bur. Standards, Circ.* 90 (issued Apr. 3, 1920).

WHITE LEAD

(BASIC CARBONATE)

General.—The theoretical composition of basic carbonate white lead* is $Pb(OH)_2 \cdot 2PbCO_3$. The analysis of this would show:

	Per cent
Total lead, calculated as PbO	86.33
Carbon dioxide, CO_2	11.35

Equivalent to:

Lead hydroxide, $Pb(OH)_2$	31.10
Lead carbonate, $PbCO_3$	68.90

It is furnished to the trade either dry or ground in oil. In the latter case, the amount of oil is generally about 8%.

The pigment of commercial white leads generally yields between 11 and 13% of CO_2. There should be no appreciable acid-insoluble material and not more than 0.75% of lead acetate. The pigment should contain at least 98% of white lead, calculated to the above formula.

Vehicle (Oil).—Pour about 50–75 grams of the thoroughly mixed material into a small beaker and weigh it in the beaker together with a stirring rod. Dry and weigh one of the specially hardened extraction thimbles with a plug of cotton wool in the end of it. Remove the cotton and fill the thimble about two-thirds full of the pigment, pouring it from the beaker by means of the stirring rod. Weigh the beaker again, and from the difference in weight obtain the amount of material taken. Plug the thimble with the cotton and place in a Soxhlet extractor. Fill the extractor about two-thirds full of ether, and let stand at least 1 hour before starting the siphoning. Then extract until no more oil is removed. Dry the thimble with the extracted pigment and weigh it.

NOTE.—When it is not necessary to determine the relative proportions of oil and pigment, the oil can be extracted more quickly by stirring some of the material up with petroleum ether, centrifuging and decanting the liquid several times until no more oil is left in the pigment.

* Also called Corroded White Lead.

Analysis of Pigment

Acid-insoluble Matter.—Dissolve 0.5 gram of the dry pigment (well mixed and ground) in hot dil. HNO_3. If an appreciable amount of insoluble material remains, filter the solution, wash the residue with hot water, ignite and weigh.

Total Lead.—Dilute the filtrate from the insoluble material to about 250 cc. and add NH_4OH until the solution is slightly alkaline. Then add dil. acetic acid in slight excess. Heat to boiling, and add a hot solution of $K_2Cr_2O_7$ in excess. Sufficient bichromate solution should be added so that when the $PbCrO_4$ settles, the supernatant liquor is distinctly yellow or orange. Boil until the precipitate settles quickly (about 2 minutes generally suffices). Filter through a weighed Gooch crucible. Wash with hot water, dry at 100° C., set the Gooch crucible in a larger platinum crucible, ignite gently, cool in a desiccator and weigh as $PbCrO_4$.

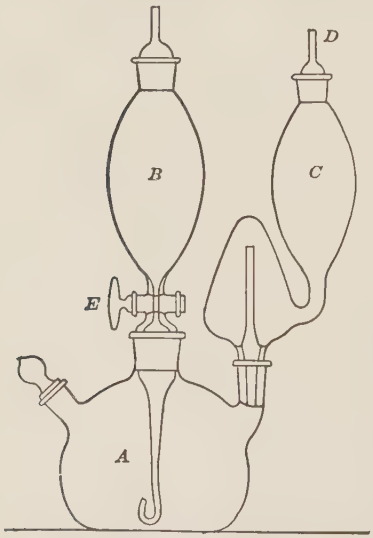


Fig. 16.—Alkalimeter for Carbon Dioxide Determination.

Carbon Dioxide.—For this determination use a Geissler alkalimeter (Fig. 16). Weigh out 5–10 grams of the dried pigment and brush it carefully by means of a funnel scoop into the lower chamber (*A*) of the alkalimeter. Add a few cc. of water and connect the acid chamber (*B*). Close the stop-cock (*E*) and fill this chamber nearly full of dil. HCl or HNO_3 (1:4). In the chamber (*C*) should be just enough conc. H_2SO_4 to make a seal. Weigh the whole apparatus. Open the stop-cock (*E*) and let the dilute acid run slowly upon the pigment. When nearly all the acid has run in, close the stop-cock. Complete the reaction by placing the whole apparatus in a beaker and setting on the steam bath. Make sure that all the pigment has been dissolved, then allow the alkalimeter to come to room temperature. Attach

a small rubber tube to the outlet of the side-arm at (*D*) and open the stop-cock. Suck air slowly and carefully through the apparatus until all the liberated CO_2 has been replaced by air; then weigh on the balance. The loss in weight is CO_2.

Lead Acetate.—Dry some of the extracted pigment at 105° C. Place a little on a watch glass and moisten with a few drops of KI solution. If acetates are present, a yellow color will form. To determine the amount, weigh 5–10 grams of the pigment into a distilling flask, add 200 cc. of water and 5 cc. of sirupy H_3PO_4 and distill until the distillate no longer comes over acid. Then titrate the distillate with 0.1 N NaOH and phenolphthalein.

1 cc. 0.1 N NaOH = 0.01897 gram $Pb(C_2H_3O_2)_2 \cdot 3H_2O$.

Calculations.—Calculate the $PbCrO_4$ to PbO. Calculate the CO_2 to $PbCO_3$. From the total $PbCrO_4$ subtract the equivalent of $PbCO_3$ and of $Pb(C_2H_3O_2)_2$ and calculate the difference to $Pb(OH)_2$.

$$PbCrO_4 \times 0.6906 = PbO.$$
$$CO_2 \times 6.0729 = PbCO_3.$$
$$PbCO_3 \times 1.2096 = PbCrO_4.$$
$$Pb(C_2H_3O_2)_2 \cdot 3H_2O \times 0.8521 = PbCrO_4.$$
$$PbCrO_4 \times 0.7464 = Pb(OH)_2.$$

CHROME YELLOW

General.—The most important yellow pigment is chrome yellow, which varies from a light yellow color to deep orange. The lighter shades generally contain $PbSO_4$ as well as $PbCrO_4$, while the deep orange contains some basic lead chromate. Pure chrome yellow should contain only $PbCrO_4$, $PbSO_4$ (or white lead) and possibly some basic lead in the darker shades. A chrome yellow should be considered adulterated if it contains anything in appreciable amount besides water-insoluble lead compounds. The following analytical method applies to the dry pigment or to the pigment of a paste after the vehicle has been removed.

Moisture.—Dry 2 grams in a watch glass or dish to constant weight at 105° C.

Note.—As the pigment of pastes is generally dried in extracting the oil, the determination of moisture in such cases is superfluous.

Insoluble Impurities.—Treat 1 gram in a beaker with 20 cc. of conc. HCl, cover and heat on a steam bath for 15 minutes. Add 100 cc. of hot water, boil (the solution should be complete), filter, wash very thoroughly* with hot water, ignite in a platinum crucible, cool in a desiccator and weigh the insoluble impurities.

If the impurities are considerable in amount, evaporate the residue twice with HF and a few drops of dil. H_2SO_4, drive off the H_2SO_4, ignite and weigh. If the insoluble impurities are mostly volatile with HF, report as silica. If the residue from the HF treatment is considerable, fuse it with $KHSO_4$ and dissolve in water containing a little HCl. Filter out, ignite and weigh any insoluble residue. If the treatment with HF was complete, this residue is probably $BaSO_4$, but it should be confirmed qualitatively.

The filtrate from the $BaSO_4$ will contain insoluble Fe_2O_3, Al_2O_3, CaO, and MgO. Iron and alumina alone indicate clay or similar mineral matter; a considerable amount of MgO generally indicates talc. It is not usually necessary to determine the insoluble Fe, Al and Mg; the difference between the $BaSO_4$ (if any) and the total insoluble may be reported as "silicious matter."

Total Lead.—Nearly neutralize the filtrate from the insoluble matter with NH_4OH, and dilute to 350 cc. Pass in a rapid current of H_2S for 10 minutes. Cover with a watch glass, place on the steam bath and let settle. Test a portion of the clear liquid for complete precipitation by diluting with an equal volume of water and passing in more H_2S. If precipitation is not complete, dilute the whole to about 500 cc. and pass in more H_2S. Finally filter out the PbS and wash rapidly with water containing a little H_2S. Dissolve the PbS with hot conc. HNO_3 containing a little bromine water, dilute to about 100 cc., filter out sulfur if necessary, cool, add 5 cc. of conc. H_2SO_4, and evaporate to strong (white) SO_3 fumes. Cool and add 100 cc. of water and 50 cc. of alcohol. Let stand 1 hour or until the $PbSO_4$ settles clear. Filter on a weighed Gooch crucible, wash with 5% H_2SO_4 and finally with alcohol, dry at 105° C., set the crucible in a larger platinum crucible, ignite until pure white, cool and weigh as $PbSO_4$.

* Incomplete washing will not only give high results but may cause serious damage to the platinum crucible.

NOTE.—In the presence of Cr the solution must be very dilute and the H_2S passed in rapidly to get a good separation.

Iron Oxide.—Boil the filtrate from the PbS until free from H_2S. Add a few drops of HNO_3 and boil again. Add a very slight excess of NH_4OH, boil, let settle, filter and wash with hot water. Save the filtrate. Dissolve the precipitate (hydroxides of Fe, Al and Cr) in HCl. Rinse into a 500-cc. volumetric flask and dilute to the mark.

To 200 cc. of the above solution, add a very slight excess of NH_4OH and then sufficient Na_2O_2 to oxidize all the Cr. Boil until all the H_2O_2 is expelled. If there is any insoluble residue filter and wash slightly. Dissolve the precipitate in dil. HCl, dilute with water, add a slight excess of NH_4OH and treat with peroxide as before. Filter, wash with hot water and add this filtrate to the previous one. Ignite the residue strongly in a platinum crucible, cool and weigh as Fe_2O_3. Calculate to percentage.

Lead Chromate.—Acidify with acetic acid the total filtrate from the Fe determination, boil until all H_2O_2 is decomposed and treat by one of the following methods. In either case divide the result by 0.4 and multiply by 100 to obtain the percentage of $PbCrO_4$.

GRAVIMETRIC METHOD.—Add a slight excess of clear lead acetate solution (a basic solution can generally be cleared up by adding a few drops of acetic acid), digest on the steam bath until the precipitate settles clear, and filter on a weighed Gooch crucible, washing with hot water; dry, set the crucible inside of a larger platinum crucible, ignite gently, cool in a desiccator and weigh as $PbCrO_4$. The precipitate should not be allowed to stand in the beaker an undue length of time after settling clear on account of the danger of becoming basic, nor should the solution be boiling when the lead acetate is added or at any time after.

VOLUMETRIC METHOD.—Cool the solution which has been freed from H_2O_2, make distinctly acid with H_2SO_4, add a measured excess of 0.1 N ferrous ammonium sulfate solution and titrate the excess of the latter with 0.1 N $K_2Cr_2O_7$, using potassium ferricyanide as an outside indicator. The end-point is the disappearance of the blue color first produced. From the amount of

ferrous ammonium sulfate oxidized, calculate the amount of $PbCrO_4$ corresponding to the chromium.

CALCULATION.—1 cc. 0.1 N $Fe(NH_4)_2(SO_4)_2 = 0.01077$ gram $PbCrO_4$.

Alumina.—Alumina is very seldom present but may be determined in an aliquot of the solution prepared above under Iron Oxide by oxidizing with Na_2O_2, filtering, rendering the filtrate slightly acid with HCl and then very slightly alkaline with NH_4OH. This precipitates $Al(OH)_3$. Filter, wash with hot water, ignite in the blast, cool and weigh as Al_2O_3. (After adding the NH_4OH, the solution should not be boiled, as some $Cr(OH)_3$ may also thus be thrown down.)

Zinc Oxide.—Into the filtrate from the original precipitate of hydroxides of Fe, Al and Cr (which should be ammoniacal) pass H_2S, heat to boiling, and filter through a hardened filter, washing with H_2S water. Dissolve the ZnS in a slight excess of HCl, dilute to 200 cc., boil off all the H_2S, add a slight excess of NH_4OH and then an excess of acetic acid. Heat to boiling and add an excess of ammonium phosphate solution. Stir thoroughly and let stand until clear; filter and wash with water on a porcelain Gooch crucible, dry, ignite and weigh as $Zn_2P_2O_7$. Calculate to ZnO.

CALCULATION.—$Zn_2P_2O_7 \times 0.5340 = ZnO$.

Lime.—(Lime is seldom present unless the material is adulterated with gypsum.) To the ammoniacal filtrate from the ZnS add an excess of hot sodium or ammonium oxalate solution and determine the CaO in the usual way.

Magnesia.—The MgO is determined in the filtrate from the CaO in the usual way by precipitating as $MgNH_4PO_4$. It is almost never present in a chrome yellow in an acid-soluble form.

Total SO_3.—Dissolve 1 gram of the pigment by heating with 20–25 cc. of HCl as described under Insoluble Impurities. Filter and wash with hot water and dilute to about 400 cc. Heat to boiling and add an excess of hot $BaCl_2$ solution, drop by drop; boil for 0.5 hour and let stand on the steam bath until the precipitate settles clear. Filter and wash with hot water; ignite in a platinum crucible and weigh as $BaSO_4$. Calculate to SO_3.

CALCULATION.—$BaSO_4 \times 0.3430 = SO_3$.

NOTE.—The solution must be kept hot and dilute to prevent contamination of the precipitate with lead.

Calculation of Results.—The $PbCrO_4$ is obtained directly. Calculate the SO_3 to $PbSO_4$ and subtract this from the total Pb calculated as $PbSO_4$. From the remainder subtract the equivalent of the $PbCrO_4$. Calculate the remaining lead to PbO and report as basic PbO; or, if carbonates are present, calculate to white lead, $2PbCO_3 \cdot Pb(OH)_2$. The small amounts of Fe_2O_3, CaO, etc., are reported as such, unless it is evident that calcium carbonate or sulfate is present.

NOTE.—Some chrome yellows contain barium phosphate, barium sulfate, or calcium sulfate in place of the $PbSO_4$; sometimes also lead citrate is used.

FACTORS.—$BaSO_4 \times 1.2991 = PbSO_4$.
$PbCrO_4 \times 0.9383 = PbSO_4$.
$PbSO_4 \times 0.7360 = PbO$.
$PbSO_4 \times 0.8526 =$ White Lead.
$SO_3 \times 2.1504 = CaSO_4 \cdot 2H_2O$.

REFERENCE.—*U. S. Bur. Chem., Bull.* 109, revised, 29.

ZIRCONIA PIGMENTS

General.—The white pigments containing zirconium encountered in this laboratory have been zirconium silicate, zirconium oxide and mixtures of these two with barium sulfate, antimony oxide and zinc oxide, together with small amounts of oxides of Fe, Al and Ti. Before attempting quantitative determinations it is advisable to make a qualitative analysis.

A

PROCEDURE FOR ZIRCONALBA

General.—The material sold under the trade name of Zirconalba we have found to have approximately the following composition:

	Per cent
Loss on ignition	14–24
Silica	15–38
Zirconium oxide	42–68
Iron oxide and alumina	None
Titanium oxide	0.35–1.00

The main constituent is probably a hydrated zirconium silicate. The following procedure has been found to give satisfactory results on material of this sort.

Loss on Ignition.—Ignite a 1-gram sample in a weighed platinum crucible for 1 hour at bright red heat; cool in a desiccator and weigh.

Silica.—Fuse a 1-gram sample with about 5 grams of $KHSO_4$ for 1 hour. Disintegrate the melt with hot 5% H_2SO_4, filter and wash with hot water on a quantitative filter. Ignite the residue and again fuse with 4 or 5 grams of $KHSO_4$. Digest this residue with hot 5% H_2SO_4, filter, wash and ignite in a weighed platinum crucible.

These two fusions remove practically everything except SiO_2. Moisten the weighed residue in the crucible with a few drops of H_2SO_4, add about 15 cc. of HF and evaporate to dryness. Ignite and weigh. The loss is SiO_2. Fuse the slight residue which remains in the crucible with about 1 gram of $KHSO_4$. This residue should be completely soluble in water if the HF treatment has dissolved all the silica; if not, repeat the HF treatment.

Add the solution of the final fusion to the two previous filtrates and dilute to 500 cc. in a volumetric flask.

Zirconium Oxide.—To an aliquot of 100 cc. of the above solution add slowly, while boiling, an excess of NH_4OH. Filter, wash with hot water, ignite strongly and weigh. This gives $ZrO_2+TiO_2+Al_2O_3+Fe_2O_3$. The last three substances are determined on separate aliquots and the ZrO_2 taken by difference.

Iron Oxide and Alumina.—To another 100-cc. aliquot of the original solution add an excess of Na_2HPO_4 solution. This precipitates phosphates of Zr and Ti,* which are insoluble in dilute acid. Heat on the steam bath for 0.5 hour, filter and wash thoroughly with hot water. Make the filtrate alkaline with NH_4OH and boil. Filter, wash with hot water, ignite in a porcelain crucible and weigh as $FePO_4+AlPO_4$. If the precipitate is less than 1% in weight, multiply by 0.474 (the average of the factors for converting $AlPO_4$ and $FePO_4$ to their oxides) and report as $Fe_2O_3+Al_2O_3$.

* If the solution has been oxidized with an excess of H_2O_2 before adding the phosphate, the titanium will not come down.

If the weight of mixed phosphates is considerable, fuse the residue with $KHSO_4$, dissolve in 5% H_2SO_4, pass through the Jones reductor and titrate with 0.05 N $KMnO_4$. Calculate the titration to Fe_2O_3 and to $FePO_4$, subtract the weight of the latter from the mixed phosphates and calculate the difference ($AlPO_4$) to Al_2O_3.

Calculations.—1 cc. 0.05 N $KMnO_4 = 0.003992$ gram Fe_2O_3.
$= 0.007544$ gram $FePO_4$.

$$AlPO_4 \times 0.4177 = Al_2O_3.$$

Titanium Oxide.—Oxidize a 50-cc. aliquot of the original solution by adding about 5 cc. of H_2O_2 (ordinary 3% solution), dilute with 5% H_2SO_4 to 100 cc. or other definite volume in a volumetric flask and compare the color with a standard titanium solution as described on page 778.

B

Procedure for Materials Containing Zirconium Silicate, Zirconium Oxide and Barium Sulfate

Loss on Ignition.—See under *A*.

Silica.—Fuse a 1-gram sample with about 5 grams of Na_2CO_3 for 1 hour in a platinum crucible. Disintegrate the melt with hot water, filter and wash thoroughly with hot water. Acidify the filtrate with HCl, evaporate to dryness in a porcelain dish and bake at 150° F. for 0.5–1 hour. Take up with 20 cc. of dil. HCl (1:1), cover the dish and digest on the steam bath for 10 minutes. Dilute, filter and wash with hot water. For accurate results, again evaporate the filtrate to dryness, take up with HCl (1:1), digest for 10 minutes, filter, (save the filtrate) and wash with hot water. Place both filters in a platinum crucible, dry, ignite and blast to constant weight. Fill the crucible about two-thirds full with HF, evaporate to dryness, ignite and again weigh. Report the loss as SiO_2. If there is an appreciable residue from the HF treatment, fuse it with $KHSO_4$, dissolve the fusion in 5% H_2SO_4 and add to the filtrate from the SiO_2 determination.

Barium Sulfate.—Ignite the washed residue from the Na_2CO_3 fusion in a platinum crucible. Add about 5 grams of $KHSO_4$ and fuse at a gentle heat, just sufficient to keep the mixture

liquid, for 3 or 4 hours. Cool and take up the fusion in 2% H_2SO_4. Any residue at this point will be $BaSO_4$ or a small amount of SiO_2. Filter, wash with hot water, ignite and weigh. Evaporate the residue with about 10 cc. of HF. Again ignite and weigh. The loss is SiO_2 which should be added to that previously determined. The residue is $BaSO_4$, which should be confirmed by qualitative test.

Zirconium Oxide.—Mix the filtrates from the Silica determination from the $KHSO_4$ fusion above and dilute to 500 cc. in a volumetric flask. Pipette out 100 cc.* and add an excess of Na_2HPO_4 solution to precipitate zirconium phosphate, which is insoluble in dilute acid. Heat on the steam bath for 0.5 hour, filter and wash thoroughly with hot water followed by 5% NH_4NO_3 solution. Dry the precipitate and separate from the paper as completely as possible. Ignite first the paper in a weighed porcelain crucible, then add the main portion of the precipitate and ignite strongly till white or grayish white. Cool in a desiccator and weigh as ZrP_2O_7. Calculate to ZrO_2.

CALCULATION.—$ZrP_2O_7 \times 0.4642 = ZrO_2$.

Iron Oxide and Alumina.—Make the filtrate from the zirconium phosphate strongly alkaline with NH_4OH and boil. Then proceed as under Iron Oxide and Alumina in *A*, unless titanium is present, in which case proceed as under *C*, described later.

C

PROCEDURE FOR MATERIALS CONTAINING SILICA AND OXIDES OF ANTIMONY, ZIRCONIUM, TITANIUM AND ZINC

Loss on Ignition.—See under *A*.

Antimony Oxide.—Fuse a 1-gram sample with NaOH in a nickel crucible. Take up the fusion in water, cool and acidify with HCl. Add 5 grams of tartaric acid and boil. This should give a clear solution. Dilute to about 500 cc. in an Erlenmeyer flask. Heat to gentle boiling and pass in a stream of H_2S until precipitation is complete. Filter off the Sb_2S_5 and determine the Sb as on page 172. Calculate to Sb_2O_4.

CALCULATION.—$Sb \times 1.2628 = Sb_2O_4$.

* If TiO_2 is present, add 5 cc. of H_2O_2 to oxidize it before adding the phosphate. In this case the titanium will come through into the filtrate.

Silica.—To the filtrate from the Sb_2S_5 add 10–15 cc. of conc. H_2SO_4 and evaporate on the hot plate to fumes of SO_3. Heat until all the tartaric acid is destroyed, adding a few drops of conc. HNO_3 from time to time and more H_2SO_4, if necessary. Finally drive off nearly all of the H_2SO_4, leaving a residue of only 2 or 3 cc. Cool and add 100 cc. of water. Heat to boiling, filter off the SiO_2, wash with hot water, ignite the residue strongly in a weighed platinum crucible over a blast lamp and weigh as SiO_2. A double evaporation is not necessary as the heating with conc. H_2SO_4 dehydrates the silica.

Zirconium Oxide.—Dilute the filtrate from the SiO_2 to 500 cc. in a volumetric flask, pipette out 100 cc. and determine zirconium as phosphate as described under *B*.

Iron Oxide and Alumina.—Pipette out another 100 cc. of the filtrate solution from the SiO_2 determination, add 2 grams of powdered NH_4Cl and a few drops of HNO_3, heat to boiling and precipitate with an excess of NH_4OH. Filter, wash with hot water, ignite the residue strongly in a platinum crucible and weigh as $ZrO_2+Fe_2O_3+Al_2O_3+TiO_2$. Save the filtrate if either Zn or Mg is present.

Fuse the above precipitate with an excess of $KHSO_4$ and dissolve in 5% H_2SO_4. Add a little H_2O_2 to the solution. If a yellow color is produced, Ti is present. If no Ti is found, pass the warm solution through a Jones reductor and titrate the Fe with 0.05 N $KMnO_4$.

If Ti is present, boil off the H_2O_2 and reduce the Fe by passing H_2S into the solution till saturated. Boil until the odor of H_2S can no longer be detected and filter, if necessary, to remove any sulfur. Cool and add 2 or 3 cc. of a saturated $HgCl_2$ solution to remove the last traces of H_2S. Then titrate directly with 0.05 N $KMnO_4$.

Subtract the amount of Fe_2O_3 above obtained, together with the ZrO_2 previously determined and the TiO_2 separately determined as described below, from the total weight of the mixed oxides. The difference is Al_2O_3.

Titanium Oxide.—To the solution after titrating the Fe (after reduction with H_2S) add about 5 cc. of H_2O_2 (ordinary 3% solution). Dilute with 5% H_2SO_4 to 100 cc. or other definite volume

in a volumetric flask and compare the color with a standard Ti solution as described on page 778.

Zinc Oxide.—To the filtrate from the mixed oxides obtained in the determination of Iron Oxide and Alumina add acetic acid in very slight excess. Heat to boiling and add slowly an excess of sodium or ammonium phosphate solution. Stir briskly until the precipitate becomes crystalline, taking care that the stirrer does not touch the sides or bottom of the beaker. Set aside for several hours, filter on a weighed Gooch crucible, wash with hot water, ignite strongly and weigh as $Zn_2P_2O_7$. Calculate to ZnO.

CALCULATION.—$Zn_2P_2O_7 \times 0.5340 = ZnO$.

OIL VARNISHES

General.—The methods of analysis for varnishes are far from satisfactory. Several methods for the determination of gums have been proposed, but none of them is reliable. It is, therefore, advisable to omit this determination and report the combined percentage of oil and gums. In case it is desired to get an approximate estimate of the gums, Boughton's method as described in Technologic Paper No. 65 of the Bureau of Standards, may be used.

Care should be used in passing final judgment on a varnish merely from chemical tests, as the gloss, working qualities and durability depend largely upon the quality of the gum used, the quality and treatment of the oil, the quality of the driers and especially upon how the varnish was prepared as regards heat, method of cooking, aging, filtering, etc.

In the manufacture of oil varnish the resins or "gums" are melted and at the proper time the oil and driers are added. The mass is mixed and heated, then cooled and thinned, filtered and run into settling tanks where it is aged. The time of heating, temperature, etc., depend upon the nature of the varnish and vary greatly for different kinds.

Many different resins are used, such as Kauri, Zanzibar, Pontianak, Manila and Colophony (rosin). Generally the harder resins are more valuable. The principal oils used are Linseed and China Wood (Tung Oil). Common thinners are turpentine and light mineral oils. Compounds of Pb and Mn (and some-

times Co) are used as driers, and if rosin is present, lime is generally added to harden it.

The following tests are of value in judging the quality of a varnish:

Appearance and Odor.—Transfer the sample, if it is in a metal container, to a glass-stoppered cylinder or bottle and note its appearance, color, transparency, body, and whether any sediment is present. The presence of light petroleum oil or wood turpentine may often be detected by the odor. After making these observations, the sample should be thoroughly mixed before making the remaining tests.

Specific Gravity.—Determine with a pycnometer, hydrometer or Westphal balance at 15.5° C.

Flash Point.—Determine the flash point in the closed cup tester (preferably the Tag tester), as described in the method for Fuel Oils (see p. 244), using a low flame. Begin testing at 65° F. A low flash point may indicate light petroleum oil. Turpentine flashes at about 93° F.

Viscosity.—The determination of viscosity is not generally necessary but may throw some light on its working qualities, particularly in comparison with other varnishes. Sufficiently accurate comparative results may be obtained by using a 100-cc. Dudley pipette and comparing with water as described in the method for Glue (p. 424). The viscosity should be run at 20° C.

Volatile Thinners.—Weigh 100 grams of the varnish into a 500-cc. flask, connect with a spray trap and a water condenser, and pass through it a current of steam, first heating the flask in an oil bath at 100° C. With the steam still passing through, raise the temperature of the bath to 130° C. Catch the distillate in weighed glass-stoppered graduates, and continue distillation until 300 cc. of water have been condensed. Do not fill any graduate above the top mark. Let the distillates stand until they separate into two layers, then read the volume of water and weigh each graduate. Subtract the volume of water and weight of empty graduates and the difference is the weight of volatile thinners. Filter the light oils through dry papers and examine for turpentine and petroleum oils. A slight error is caused by the solubility of turpentine in water; this amounts to about 0.3–0.4 cc. for each 100 cc. of water.

When sufficient varnish is available, it is well to take another portion and distill without steam or spray trap, placing the weighed flask in an oil bath. Note the temperature of the bath at which distillation begins, and continue distillation at a temperature of 185° C. in the oil bath, finally raising the temperature to 200° C. This method generally tends to give lower results on volatile oils than the steam-distillation method; but the distillate can be tested for water-soluble volatile liquids, which would be lost by the steam distillation.

Fixed Oils and Gums.—The percentage of fixed oils and gums is obtained by subtracting the percentage of volatile thinners from 100. A check upon this determination is obtained by weighing the residue from the dry distillation. In case an actual determination of the approximate amount of gums is required, use Boughton's method previously referred to.

Acid Number.—Determine the acid number as described on page 311, using 10 grams of the varnish.

Rosin.—After determining the acid number, decant the alcohol, evaporate and apply the Liebermann-Storch test; or test the original varnish as follows:

Pour about 5 cc. into a separatory funnel, add an equal volume of CS_2, shake and add 10 cc. of acetic anhydride. Let stand until completely separated. Draw off the lower layer of anhydride. Pour 1–2 cc. of this into an inverted crucible cover, add carefully by means of a stirring rod 1 drop of dil. H_2SO_4 (1 : 1) to the edge of the cover so that it will mix slowly with the anhydride. If rosin is present, a characteristic fugitive violet color will result. Do not confuse this with the brown or reddish-brown color often given by other gums.

Ash.—Determine the ash in 10 grams, using a quartz or porcelain dish and carrying out the incineration at a low heat, best in a muffle. Determine the reaction of the ash to litmus paper and make a qualitative analysis. It is frequently well to make a quantitative determination of CaO, a large amount of which indicates rosin. It is sometimes advisable to determine the percentages of Pb and Mn. Some Pb will, however, be lost in the ashing, and if a correct determination is required, proceed as under the determination of Drying Salts in Japan Driers (see p. 288).

Examination of Films.—Flow the varnish on a carefully cleaned plate of glass and let dry at room temperature in a vertical position. Note the time required for the varnish to "set to touch," *i.e.*, to lose its tackiness when touched lightly with the finger, and also the time required for drying hard. After 24 hours examine the film, noting transparency, hardness, elasticity and tendency to dust by scratching. After thoroughly drying, immerse the plate in water overnight, dry without heat and note the appearance.

Practical Tests.—The working quality of a varnish must be determined by application on wood and it is best to make this test on well-seasoned and perfectly smooth white pine. Apply a thin coating of the varnish, let dry and sandpaper down smooth and then apply the coat to be tested. Observe how the varnish works under the brush, character of coat, etc. This panel, after drying, may be used for further testing as to whether the varnish will stand rubbing, etc.

NOTES.—(1) "Short oil" varnishes contain considerably more resin than oil, and "long oil" varnishes *vice versa*.

To test, place 10 cc. of varnish in a small beaker and add 50 cc. of benzine which has been previously cooled to 5° C. If the varnish is "short oil," the gums will be partly precipitated and light in color; if a "long oil" varnish, there will be very little precipitation and the solution will be dark-colored. Interior varnishes should be "long oil" for the best quality of work and exterior varnishes should always be "long oil." Rubbing varnishes should be "short oil."

(2) The U. S. Government Specification for Interior Varnish, 1922, requires:

(*a*) Appearance: Clear and transparent.

(*b*) Color: Not darker than a solution of 3 grams of $K_2Cr_2O_7$ in 100 cc. of pure conc. H_2SO_4.

(*c*) Flash point (closed cup): Not below 85° F.

(*d*) Non-volatile matter: Not less than 45% by weight after heating at 220–230° F. for 3 hours.

(*e*) Set to touch: In not more than 4 hours (at 70–90° F.).

(*f*) Dry hard: In not more than 24 hours (at 70–90° F.).

(*g*) Dry to rub: In not more than 48 hours.

(*h*) Toughness: Film on metal must stand rapid bending over a rod $\frac{1}{8}$ inch in diameter.

(*i*) Working properties: Must have good brushing, flowing, covering, leveling, and rubbing properties; and must show no impairment of luster or other defect when used where natural or illuminating gases are burned or when subjected to air currents during the process of drying or application.

(*j*) Water resistance: The dried film must stand application of cold water for not less than 18 hours without whitening or showing other visible defect.

REFERENCES.—*Bur. Standards, Tech. Paper* 65; *Bur. Chem., Bull.* 109, revised; Holley and Ladd: "Mixed Paints, Color Pigments and Varnishes." *Bur. Standards, Circ.* 117.

JAPAN DRIERS

General.—The analysis of Japan driers is in general conducted in the same way as that of Oil Varnish, with the following modifications:

Volatile Thinner.—Weigh quickly 5 grams from a weighing bottle into a glass Petri dish, evaporate on the steam bath and then dry for 3 hours at 100° C. Cool and weigh. The loss represents the amount of volatile thinner, which is generally about 65%.

Drying Salts.—The most generally used driers are linoleates, resinates or borates of Pb and Mn, or mixtures of these substances. As a rule, in light Japans manganese borate is used; in dark Japans, manganese oxide; and medium Japans, lead oxide. The most common composition is a mixture of Mn borate and PbO. Zinc is now seldom used. Qualitative tests for Mn, Pb and Zn are generally sufficient, but if a quantitative determination is desired proceed as follows:

Place 25 grams in a 250-cc. Erlenmeyer flask and add 25 cc. of a mixture of equal parts of gasoline and turpentine. Add 50 cc. of dil. HNO_3 (1 : 1) and let stand 1 hour, shaking every 10 minutes. Then immerse in hot water and shake gently. Keep away from any flame. When thoroughly hot, mix with a circular motion to get rid of most of the gasoline. When cool, pour into a separatory funnel, draw off the lower aqueous layer into a casserole and wash the upper oily layer four or five times with warm water. Add the washings to the casserole and evaporate to dryness under the hood. Dissolve by warming with dil. HNO_3. Filter into a 250-cc. volumetric flask and make up to the mark.

LEAD.—To 100 cc. of the above solution add 5 cc. of conc. H_2SO_4 and evaporate on the hot plate to strong fumes. Cool, add 100 cc. of water and heat to boiling to dissolve anhydrous $FeSO_4$ if present. Let stand until cooled and the precipitate has settled clear. Filter on a Gooch crucible and wash with 5% H_2SO_4. Transfer the filtrate, which should be about 150 cc., to

a beaker and wash the $PbSO_4$ on the Gooch crucible with 50% alcohol. Do not collect the aloholic filtrate in the main body of the filtrate as it is used merely to wash out the acid from the $PbSO_4$. Dry the Gooch crucible and contents and place in a larger platinum crucible. Ignite gently, cool in a desiccator and weigh as $PbSO_4$. Calculate to PbO.

CALCULATION.—$PbSO_4 \times 0.7360 = PbO$.

ZINC.—If present, Zn may be determined in the filtrate from the $PbSO_4$. To the filtrate in the beaker add 50 cc. of 30% NaOH solution and electrolyze as described under Zinc on page 183, finally weighing as metallic Zn.

MANGANESE.—The Mn will be present as hydroxide in the solution after electrolysis of the Zn. Dilute this solution to about 300–400 cc., filter, and wash with hot water. Wash into a 200-cc. Erlenmeyer flask with 50 cc. of warm dil. HNO_3 (1:3), cool, add about 0.5 gram of sodium bismuthate and proceed as described under Manganese on page 136.

NOTES.—(1) The following specifications of the P. & R. Railroad, 1906, will give an idea of the requirements of a good Japan.

The material desired consists of a pure turpentine hardener and oil drier, conforming to the following:

(*a*) When equal parts by weight of the Japan and of pure turpentine are thoroughly mixed and poured over a slab of glass, which is then placed nearly vertical at a temperature of 100° F., with a free access of air but not exposed to draft, the coating shall be hard and dry, neither brittle nor sticky, in not exceeding 12 minutes.

(*b*) When thoroughly mixed with pure raw linseed oil at the ordinary temperature in proportions of 5% by weight of Japan to 95% by weight of raw linseed oil, no curdling shall result, nor any marked separation or settling on standing.

(*c*) When the above mixture is flowed over a slab of glass, which is then placed nearly vertical at a temperature of 100° F., with free access to air but not exposed to draft, the coating shall dry throughout, neither brittle nor sticky, in not exceeding 2 hours.

(*d*) When 5 cc. of the Japan are poured into 95 cc. of pure turpentine at the ordinary temperature, and thoroughly shaken, a clear solution shall result, without residue, on standing 1 hour.

(*e*) After evaporation of the turpentine, the solid residue must be hard and tough, and must not "dust" when scratched with a knife.

(*f*) Benzine or mineral oil of any kind will not be permitted.

(2) The U. S. Government Specification is as follows:

Japan drier must not flash below 85° F. (closed tester), must be composed of lead, manganese, or cobalt, or a mixture of any of these elements combined

with a suitable fatty oil, with resins or "gums" and mineral spirits or turpentine, or a mixture of these solvents, and free from sediment or suspended matter. When flowed on metal and baked for 2 hours at 212° F. it must leave an elastic film. It must mix with pure linseed oil in the proportions of 1 volume of drier to 19 volumes of oil without curdling and the resulting mixture when flowed on glass must dry in not over 18 hours. When mixed with pure raw linseed oil in the proportion of 8 parts of oil to 1 part of drier by volume, the resulting mixture must not be darker than a solution of 6 grams of $K_2Cr_2O_7$ in 100 cc. of pure conc. H_2SO_4.

REFERENCES.—*Bur. Standards, Tech. Paper,* 65; *Bur. Chem., Bull.* 109, revised; Holley and Ladd: "Mixed Paints, Color Pigments and Varnishes;" *Bur. Standards,* Circ. 105.

SHELLAC AND SHELLAC VARNISHES

General.—Dry shellac occurs on the market in 2 forms, orange shellac and bleached shellac. There are many different grades of orange shellac. Bleached shellac, however, is generally of a high grade of purity. In making shellac varnishes, the dry lac is dissolved in alcohol, generally in the proportions of about 5 lbs. of the shellac to a gallon of alcohol. Formerly methyl alcohol was almost universally used but now denatured alcohol is largely employed.

SAMPLING OF DRY SHELLAC

Bleached shellac is sold in 3 forms,—(1) as hanks or bars containing approximately 25% of water, (2) as ground bleached shellac in pulverized form with about the same water content, (3) as bone-dry or kiln-dried shellac. The latter is prepared by drying the ground bleached shellac in the air or in vacuum driers at moderate temperatures. It may contain up to 10% of water or more.

In sampling bone-dry bleached shellac take a fairly large portion (about 1 pound) from different parts of the barrel and grind finely by running quickly through a coffee mill. No attempt should be made to sieve it. Mix rapidly and transfer to a Mason jar with a screw cap and a rubber ring seal. The jar should not be more than $\frac{2}{3}$ full, leaving room for a thorough mixing by shaking the contents. Keep in a cool place and test as promptly as possible. If too warm, the shellac may become partly caked, in which case the lumps must be broken up by shaking the bottle.

In sampling bars or hanks, it is recommended that a whole hank be taken. Crush and grind as rapidly as possible. Ground bleached may be treated as above, bearing in mind that the large amount of moisture present makes rapid handling imperative.

Analysis of Dry Shellac

Moisture.—Both the orange and bleached shellac give off volatile matter at temperatures approaching 100° C. Bleached shellac alters chemically at this temperature, losing its solubility in alcohol. For these reasons the usual methods of determining water by heating in an air bath at 100–110° C. are not applicable.

Method No. 1.—Weigh 5–10 grams of the sample in flat-bottomed dishes about 4 inches in diameter or in watch glasses ground to fit and provided with a clamp. Then place the shellac in a desiccator freshly filled with conc. H_2SO_4. The contents of the dish should be spread out in a thin layer to expose as large a surface as possible. Exhaust the desiccator by a vacuum pump as completely as possible. With a good vacuum (3-mm. pressure or better) constant weight will be obtained in between 24 and 48 hours. Absolutely dry bleached shellac is quite hygroscopic and the final weight should be taken as rapidly as possible.

Method No. 2.—The same results may be obtained by drying the shellac in a well-ventilated air bath for 3–6 hours at 100–110° F. (38–43° C.). One or two electric light bulbs provide a convenient source of heat. The temperature should not be allowed to rise above 43° C., otherwise sintering may occur and retard drying. With poorly ventilated ovens the drying may take much longer. Completeness of drying should be ascertained by continuing the treatment to constant weight. (Check the accuracy of results obtained in the oven by comparison with a test made in a vacuum desiccator before relying exclusively on the oven.)

Rosin.—Introduce about 0.200 gram of the shellac (0.400 gram of bleached shellac) finely ground, into a 250-cc. dry bottle of clear glass with a ground-glass stopper; add 20 cc. of special glacial acetic acid (see note 3) and warm the mixture gently until solution is complete (except for wax). A pure shellac is rather difficult of solution. Solution is quicker according to the pro-

portion of rosin present. Add 10 cc. of $CHCl_3$ and cool the solution to 21–24° C. Hold the temperature well within these limits during the test. Add 20 cc. of Wijs solution from a pipette or burette having a rather small delivery aperture. Close the bottle, stand in a dark place, and note the time. It is convenient to keep the bottles during the test partly immersed in water, kept as nearly as possible between 22–23° C.

Pure shellac will scarcely alter the color of the Wijs solution. If in small amount, rosin will produce a slowly appearing red-brown color; in large amount, rosin causes an immediate coloration, increasing in intensity as time passes. At the end of *1 hour* add 10 cc. of 10% KI solution and titrate immediately with 0.1 N sodium thiosulfate solution; 25–30 cc. may be run in immediately, unless the shellac is very impure, and the remainder added gradually with vigorous shaking. Just before the end, add a little starch solution. The end-point is sharp, as the reaction products of shellac remain dissolved in the $CHCl_3$. Disregard any color returning after a half minute or so.

Run a blank determination with 20 cc. of Wijs solution, 20 cc. of acetic acid, 10 cc. of $CHCl_3$ and 10 cc. of 10% KI solution. The blank is necessary on account of the well-known effect of temperature changes on the volume and possible loss of strength of the Wijs solution.

Subtract the titration of the sample from that of the blank and calculate the iodine number of the sample (percentage of I absorbed). From this calculate the percentage of rosin.

CALCULATION.—Let Y = percentage of rosin;
A = iodine number of mixture;
M = 18,* iodine number of shellac;
N = 228, iodine number of rosin;

then $$Y = 100\frac{(A-M)}{(N-M)}.$$

1 cc. 0.1 N thiosulfate = 0.01269 gram Iodine.

NOTES.—(1) In the case of grossly adulterated samples or in the testing of pure rosin, it is necessary to use, instead of the 0.2 gram of material, a smaller amount, say 0.15 gram, or even 0.1 gram, in order that the excess of iodine monochloride may not be too greatly reduced, as the excess of halogen is one of the factors in determining the amount of absorption. In case less

* For bleached shellac use 10 instead of 18.

than 25 cc. of thiosulfate solution are required, another test should be made, using a smaller amount of the shellac to be tested. In the case of bleached shellac, 0.4 gram should be taken.

(2) The time and temperature are very important factors. Variations from the conditions prescribed lead to unreliable results.

(3) The strength of the glacial acetic acid used in dissolving the shellac, and also in the Wijs solution, is equally important and *must* be maintained within the required limits.

The strength of acid adopted is 98.8–99.1%, with a melting point of 14.7–15° C., as determined by the Titer Method (see p. 312).

(4) In weighing shellac, some difficulty is at times experienced on account of its electrical properties; in very dry weather it may be found that the necessary handling to prepare it for weighing has electrified it and that it may be necessary to leave it on the balance pan at rest for a few minutes before taking the final weight.

(5) The following table shows how the iodine number may be interpreted in judging the quality of the shellac:

TABLE XI—QUALITY OF SHELLAC AS INDICATED BY IODINE NUMBER

Iodine Number		Rosin, *Per Cent*	Quality
Orange Shellac	Bleached Shellac		
18 or less	10 or less	None	Good
18–23	10–15	0–2.5	Fair
23–28	15–21	2.5–5	Poor
28–34	21–26	5–7.5	Bad
Over 34	Over 26	Over 7.5	Grossly adulterated

(6) Orange shellac having an iodine number of 23 begins to show rosin by the acetic anhydride test (see p. 477.).

(7) The iodine number of bleached shellac is less than that of crude shellac. Bleached shellac of good color will generally run about 8. Anything over 10 would point to adulteration. The values 10 and 228 for shellac and rosin should be used on bleached samples.

(8) The above method is the one recommended by the Committee on Uniformity in Technical Analysis, American Chemical Society, in 1907 and adopted as standard in 1917 by the American Society for Testing Materials.

Alcohol-insoluble Matter.—Add to 1 gram of the shellac 60 cc. of 95% alcohol (specially denatured alcohol Formula No. 30 may be used), heat to boiling and filter on a Gooch crucible. Wash with about 60 cc. of boiling 95% alcohol until the washings are colorless, dry at 100° C., cool in a desiccator and weigh the insoluble matter.

NOTE.—In the case of bleached shellac the sample must be dried, since the water present may dilute the alcohol to a point where solution is not complete. As prolonged heating at a temperature of 38–43° C. may render the shellac partly insoluble, a separate portion should be dried for this determination by exposing to the air in a thin layer without the application of heat.

ANALYSIS OF SHELLAC VARNISH

Specific Gravity.—Determine the sp. gr. at 15.5° C. with the Westphal balance or pycnometer, as may be most convenient. (The Westphal balance does not give accurate results if there is any suspended matter.)

Total Solids.—Weigh by difference from a weighing bottle 5–10 grams into a flat evaporating dish 2.5–3 inches in diameter, evaporate off the alcohol at a low temperature and finally dry in an oven at 40° C. to constant weight. (See under Moisture in Dry Shellac.)

Rosin.—Determine the iodine number of the dried residue and calculate the percentage of rosin as described in the analysis of Dry Shellac above. The residue must be entirely free from solvent which might affect the iodine number determination.

Examination of Solvent.—Distill a portion of the original nearly to dryness, but not far enough to decompose the shellac, and note the temperature at which the solvent comes over. Determine the sp. gr. at 15.5° C. of the latter, evaporate a portion on filter paper or blotter and note the odor of the first and last portions. In the case of denatured alcohol, the first odor is methyl alcohol and the final odor ethyl alcohol. The boiling point will also indicate whether the solvent is wood alcohol or denatured.

Calculate the pounds of dry gum shellac per gallon of the solvent.

CALCULATION.—Multiply the sp. gr. of the original by 8.33. This gives the weight per gallon of the varnish (A). This multiplied by the percentage of total solids, expressed as a decimal, will give the pounds of dry shellac per gallon of the varnish (B). Subtract (B) from (A) and the difference is the weight of solvent per gallon of varnish (C). Divide (C) by the sp. gr. of the solvent times 8.33 and call this (D). Then (B) divided by (D) will give the pounds of dry shellac per gallon of solvent.

If the sp. gr. of the original varnish is not known, use the formula $X = \frac{AB}{100 - B}$,

where X = pounds of shellac per gallon of alcohol,
A = weight in pounds of 1 gallon of solvent,
and B = percentage of total solids.

If only approximate results are desired, it is safe to assume that the solvent weighs 6.8 lbs. per gallon.

References.—A. C. Langmuir: "The Determination of Rosin in Shellac," *J. Soc. Chem. Ind.* **24,** 12 (1905).

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BLACK AIR-DRYING INSULATING VARNISH AND BLACK BAKING INSULATING VARNISH

Electric Railway Specifications

General.—The materials which these specifications cover are insulating varnishes for armatures, field coils, etc., in suitable form for use as received. They are a combination of asphalts and drying oils as a base, with a solvent, preferably hydrocarbon, such as benzine or naphtha. It is aimed to obtain a product which, under the effects of the continued heat of normal operating conditions, shall show the least loss of plasticity or lowering of its dielectric strength. It must not be sufficiently fluid under these conditions to be forced out of the coils.

Quality of Base.—The base must contain no pigment of any kind. (It should show no significant residue insoluble in benzene or CCl_4.) It must be entirely non-volatile and after application as a coating, evaporation of solvent and drying, must become a solid that is not sufficiently soft to flow at 100° C.

Quality of Solvent.—The solvent must not contain any alcohol or other electrically conductive material. It must be entirely volatile without residue at 100° C.

Amount of Solvent.—The air-drying varnish should not contain more than 60% by weight of solvent, and the baking varnish not more than 50%, when tested as follows:

Place 400 cc. of water in a liter distilling flask. Pour in 100 grams of the varnish and distill with steam. Continue the distillation until no more volatile oil distills over, taking care that there is always some water in the distilling flask so that the temperature does not rise appreciably above 212° F. Collect the distillate in a weighed graduated cylinder and weigh it, subtracting the volume of water distilled with it; or, measure its volume, determine its sp. gr. and calculate the weight.

Drying Test.—Air-drying Varnish.—Dip a piece of clean window glass in the varnish and dry in a vertical position at room temperature (70° F.). It should be set firmly in 1 hour and become free from tackiness in not more than 3 hours.

Baking Varnish.—See under Flexibility below.

Flexibility.—Place some of the varnish in a shallow pan and dip in it, one at a time, several sheets of glassine paper about 1 foot square. Hang the sheets up and let them dry perpendicularly overnight.

Air-drying Varnish.—When thoroughly dry the sheets should be flexible and should withstand ordinary bending without any of the varnish cracking, flaking or breaking off.

Baking Varnish.—Bake the sheets for 10 hours at 100° C. They should then withstand bending back flat on themselves without any cracking. Continue the baking for 10 days. They should still be flexible and withstand ordinary bending without cracking.

Dielectric Strength.—Use the above sheets for testing, unbaked sheets in the case of air-drying varnish and sheets baked 10 days at 100° C. in the case of the baking varnish. Apply an alternating current at low voltage and raise gradually until puncture occurs. Make as many tests as possible on each sheet and report the final figure as the average of at least 10 breakdowns. Also make at least 10 micrometer measurements to obtain the average thickness of the varnish film. The varnish should have a dielectric strength of at least 1000 volts for each mil of thickness.

Oil Resisting Properties.—Take a piece of ribbon copper, 4 inches long and 2 inches wide, and dip for 3.5 inches of its length

in the varnish. Let drain for 15 minutes. Place in a baking oven and bake until thoroughly dry (20–24 hours at 100° C.). With a pair of heavy scissors cut 0.5 inch off the bottom so as to remove the bead and all thickening of the coat. Also trim 0.25 inch off each side of the copper for its full length. Take a dish (metal or enamel ware) and fill it about 4 inches deep with water. On top of this pour a layer of about 0.5 inch of fairly heavy engine oil. Place the coated sheet of copper in this mixture of oil and water until the oil comes to about the middle of the coat of varnish. Then boil the mixture vigorously. At the end of every 15 minutes or so remove the piece and see whether the varnish has suffered any injury. The coating should withstand 2 hours' boiling without any effect and should withstand 4 hours' boiling without any material deterioration.

CHAPTER VII

ANALYSIS OF OILS, FATS, WAXES, AND SOAPS

ANIMAL AND VEGETABLE OILS AND FATS

General.—The usual determinations on materials of this class are specific gravity, refractive index, iodine number, saponification number and free fatty acid; and, in the case of fats, melting point. On commercial oils and fats, assumed to be true to name and free from adulteration, determinations of moisture and volatile matter, insoluble impurities, and unsaponifiable matter (often termed in the trade the "M. I. U. Test") are usually required. Certain other tests are often of value in the case of particular oils or in attempting to identify mixtures.

In this method are collected general procedures for such tests as are standard. In the case of individual oils, the special method for that particular oil should be consulted. A table of the so-called "constants" of various oils and their fatty acids is given on pages 300–307 (Table XII).

Preparation of Sample.—In the case of solid fats, melt and filter, using a hot-water funnel. Make analyses on the melted homogeneous mass. Filter oils which are not clear. Keep samples in a cool place protected from light and air to avoid becoming rancid. It is best to weigh out at once as many portions as are needed for the various determinations, using a small beaker or weighing burette.

NOTE.—On commercial oils and fats where moisture, etc., is desired, the sample may be *softened* by gentle heat if necessary, but should not be melted before making the determinations. When sufficiently softened, mix thoroughly by stirring.

Specific Gravity.—AT 15.5° C.—Determine the sp. gr. at 15.5° C. (60° F.) with a pycnometer or Westphal balance. The pycnometer should be standardized with distilled water at the same temperature. The Westphal balance should read 1.0000 in distilled water. If the reading differs from this, divide the

reading in oil by the reading in distilled water to get the correct sp. gr. of the oil.

At Temperature of Boiling Water.—Fill a weighed sp. gr. bottle (25–50 cc.) with freshly boiled hot water. Place in boiling water and boil rapidly for 30 minutes. Replace any evaporation from the bottle by the addition of boiling water. Then insert the stopper, previously heated to 100° C., remove the bottle, cool and weigh.

Dry the bottle at 100° C., fill with the dry, hot, freshly filtered fat, entirely free from air bubbles. Immerse in boiling water for 30 minutes. Insert the stopper previously heated to 100° C., cool and weigh. Divide the weight of fat by the weight of water previously found to obtain the sp. gr.

Notes.—(1) Instead of standardizing the bottle with boiling water, the following formula may be used for calculating the weight of water at 100° C. from the weight at some other temperature:

$$\text{Wt. at } 100^\circ \text{ C.} = W\frac{D}{d}[1+0.000026\ (100-t)]$$

$$=\frac{WD}{d}(1.0026-0.000026t);$$

where t = temperature at which water is weighed;
D = density of water at 100° C.;
d = density of water at t° C.;
and W = weight of water at t° C.

(2) The bottle with contents should always be weighed at room temperature.

Refractive Index.—Place the instrument so that diffused daylight or any form of artificial light can be used for illumination. Circulate through the prisms a stream of water at constant temperature. For fats, the standard temperature is 40° C.; for oils it may be 15, 20 or 25° C., depending on circumstances.

With Abbé Refractometer.—Open the double prism by means of the screw head and place a few drops of oil on the prism. Close the prisms firmly by tightening the screw head. Let stand a few minutes to come to uniform temperature. Move the alidade on the side scale backward or forward until the field of vision is divided into light and dark portions. Rotate the screw head of the compensator until a sharp colorless line is obtained between the fields, then adjust this line so that it falls on the point of intersection of the 2 cross-hairs. Read the refractive index directly on the scale.

TABLE XII—PRINCIPAL CONSTANTS OF OILS, FATS AND WAXES—ORIGINAL OIL

			Specific Gravity, H_2O @ 15.5°		Solidifying Point ° C.	Melting Point, ° C.	Saponification Value	Iodine Value	Acetyl Value	Unsaponifiable Matter, %	Refractive Index, 15.5° C.	
			100° C.	15.5° C.								
1	Acorn Oil	C	.....	0.916	+10	.....	199.3	100.7	.....	.....	1.4731	1
2	Almond Oil	C	.....	.914-.920	−10 −21	.....	189.5-195.4	93-101.9	5.8	.....	.....	2
3	Anchovy Oil	D	.....	.....	.....	.....	188.1	152.4-169.3	.....	.....	.....	3
4	Apricot Kernel Oil	C	.....	.917-.920	−20	.....	188-198.2	96-108.7	.....	.....	1.4712 @ 20°	4
5	Arachis Oil (Peanut)	C	0.867	.918-.926	−25 +3	.....	185.6-197	83.3-105	9.06	0.5-0.9	1.4731	5
6	Bear Oil	M	.....	.913-.921	.....	.....	194.8-203.4	80.4-107	.....	.....	.....	6
7	Beechnut Oil	B	.....	.920-.923	−17	.....	191.1-196.3	111.2-120.1	.....	.....	.....	7
8	Beef Marrow	M	.....	.931-.938	29 31	37 45	195.8-199.6	39.2- 55.4	4.2	.....	.....	8
9	" Tallow	M	.....	.943-.952	27 35	42 48.5	193.2-200	35.4- 47.5	2.7-8.6	.....	1.4510 @ 60°	9
10	Beeswax	P	.818-.827	.959-.975	60.5 62.4	62.5 70	87.8-107	8.3-11	15.2	52.4-56	.....	10
11	Ben Oil	C	.....	.913-.920	0 8.8	.....	184.6-187.7	72.2-11.26	.....	1.7-2.7	.....	11
12	Bone Fat	M	.....	.914-.916	15 17	21 22	184-195	46.3-55.8	11.3	0.5-1.8	.....	12
13	" Oil	I	.....	.....	.....	.....	.....	66-70	.....	.....	.....	13
14	Borneo Tallow	K	.892	.....	22	31 45	191-196	15-31	.....	.....	.....	14
15	Bottlenose Oil	N	.827	.879-.881	.....	.....	121.5-135.9	67.1- 88.5	4.1-6.4	32-42	.....	15
16	Brazilnut Oil	B	.....	.918	0	.....	193.4	90.6-106.2	.....	.....	.....	16
17	Butter Fat	M	.865-.870	.936-.940	19 23	28 34.7	220-233	25.7- 50.3	1.9-8.6	.....	1.4590-1.4620 @ 25°	17
18	Cacao Butter	K	.857	.950-.976	21.5 27.3	28 34	192-202	32.8- 41.7	2.8	.....	1.4565-1.4598 @ 40°	18
19	Calophony (Rosin)	..	.....	1.045-1.085	.....	70 140	147-194	220 (Wijs)	.....	5.0-15.2	.....	19
20	Calophyllum Oil	C	.....	.931	3	8	196	86-92.8	.....	.....	.....	20
21	Cameline Oil	B	.....	.920-.926	−18	.....	188	135.3-142.4	.....	.....	.....	21
22	Canari Oil	C	.....	.....	.....	18 28	193.5-194.3	64.7- 65.6	8.4-16.4	0.44	.....	22
23	Candlenut Oil	A	.....	.920-.926	.....	below −18	184-192.6	163.7	8.86	.....	.....	23
24	Carapa Fat	K	.....	.912-.930	8 26	15 36	195-201	65-83.7	.....	1.5-3.7	.....	24
25	Carnaüba Wax	O	.841	.990-.999	80 87	83 91	78.4- 88.3	13.2- 13.5	55.2	54-55	.....	25
26	Castor Oil	C	.909	.960-.968	−10 −12	.....	176-7-186.6	81.5- 90.6	150	0.3-0.4	1.4795-1.4803	26
27	Cedar Nut Oil	A	.....	.930	−20	.....	191.8	149.5-159.2	82(?)	.....	.....	27
28	Ceresin	S	.770	.918-.922	47 70	61 80	.....	.....	.....	.....	.....	28
29	Chaulmoogra Fat	K	.....	.951 @ 25°	.....	.....	204-213	90.4-104.4	.....	.....	.....	29
30	Cherry Kernel Oil	C	.....	.923-.928	−19 −20	.....	193.4-195	110.8-114.3	.....	.....	.....	30
31	" Laurel Oil	C	.....	.923	−19 −20	.....	194	108.9	.....	.....	.....	31
32	Chicken Fat	M	.....	.924	21 27	33 40	193.5	66.7	.....	.....	.....	32
33	Chinese Wax	P	.....	.970	80.5 81	80.5 83	80.5- 90.3	1.4	.....	49.5	.....	33
34	" Wood Oil	A	.....	.940-.945	.....	.....	190.7-192	162.8-173.7	.....	.....	.....	34
35	Chrysalis Oil	I	.910 @ 40°	.....	7 10	.....	190-194	116-118	.....	2.6-4.9	.....	35
36	" " Japanese	I	.....	.928	.....	.....	194	132	19.7	1.6	1.4757 @ 20°	36
37	Cocoanut Fat	K	.874	.926	14 23	23 27	246.2-268	8-10	0.9-12.3	0.18-0.30	1.4410 @ 60°	37
38	Codliver Oil	E	.874	.923-.930	0 −10	.....	168-193	135-181	4.8	0.5-5.3	1.4800-1.4852	38
39	Coffee Berry Oil	C	.....	.951-.953	3 6	8.9	165.1-177.5	85.0- 87.3	.....	.....	1.4777 @ 25°	39
40	Cottonseed Oil	B	.867	.922-.926	3 4	.....	191-196.5	100.9-116.9	7.6-18.6	.....	1.4737-1.4757	40

TABLE XII—PRINCIPAL CONSTANTS OF OILS, FATS AND WAXES—INSOLUBLE FATTY ACIDS

			Specific Gravity		Solidifying Point ° C.	Melting Point ° C.	Saponification Value	Iodine Value	Titer Test ° C.	
			at 100° C. (H_2O @ 15.5°)	at 15.5° C.						
1	Acorn Oil	C	.....	.....	.....	.....	.....	.....	.....	1
2	Almond Oil	C	.....	.....	5	13 14	204	93.5–96.5	9.5–11.8	2
3	Anchovy Oil	D	.....	.....	.....	.....	.....	.....	.....	3
4	Apricot Kernel Oil	C	.....	.919–.920	0	2.3 18.0	194	99.8–103.8	.....	4
5	Arachis Oil (Peanut)	C	.846	.....	23.8 –31	27.7 35	201.6	95.5–103.4	28.1–28.2	5
6	Bear Oil	M	.....	.935	36.1	30.5 37.5	203	45.5–65	.....	6
7	Beechnut Oil	B	.....	.....	17	23 24	.....	114	.....	7
8	Beef Marrow	M	.....	.930–.940	38 40	45 46	204 5	55.5	38	8
9	" Tallow	M	870 (H_2O @ 100°)	.....	.....	43 47	197.2–201.6	25.9–41.3	43.45	9
10	Beeswax	P	.....	.....	.....	67.2	.....	.....	.....	10
11	Ben Oil	C	.....	.....	.....	.....	.....	.....	32–38.7	11
12	Bone Fat	M	.....	.....	28	30	200	55.7–57.4	42.5	12
13	" Oil	I	.....	.....	.....	.....	.....	.....	.....	13
14	Borneo Tallow	K	.....	.....	51 54	53.5 55	.....	31	.....	14
15	Bottlenose Oil	N	.....	.....	10.1	10.3 16.8	.....	82.2–83 3	8.3–8.8	15
16	Brazilnut Oil	B	.....	.....	31.1 32.3	28 30	.....	108	31.1–32.3	16
17	Butter Fat	M	.907–.915@(37.75°)	.....	33 38	38 45	210–220	28–31	36.5–37.5	17
18	Cacao Butter	K	.....	.....	46 51	48 53	190	32.6–39 1	48–49.6	18
19	Calophony (Rosin)	..	.....	.....	.....	.....	.....	.....	.....	19
20	Calophyllum Oil	C	.....	.....	33	38	194	92 2	.....	20
21	Cameline Oil	B	.....	.....	13 14	18 20	.....	136 8	.....	21
22	Canari Oil	C	.....	.....	.....	40.4	205	67.2	37–41	22
23	Candlenut Oil	A	.....	.....	13	20 21	.....	142.7–185.7	.....	23
24	Carapa Fat	K	.....	.....	.....	.....	192–207	.....	34–38	24
25	Carnaüba Wax	O	.....	.....	.....	85	.....	.....	.....	25
26	Castor Oil	C	.896	.951	3	13	.....	86 6–88 3	.....	26
27	Cedar Nut Oil	A	.....	.....	11.3	.....	193	161.3	.....	27
28	Ceresin	S	.....	.....	.....	.....	.....	.....	.....	28
29	Chaulmoogra Fat	K	.....	.....	.....	44 45	215	86–103	39.6	29
30	Cherry Kernel Oil	C	.....	.....	13 15	16 21	189	104.3–114.3	.....	30
31	" Laurel Oil	C	.....	.....	15 17	20 22	.....	112.1	.....	31
32	Chicken Fat	M	.....	.928	32 34	38 40	200.8	64.6	.....	32
33	Chinese Wax	P	.....	.....	.....	92.2	.....	.....	.....	33
34	" Wood Oil	A	.....	.....	.....	.....	.....	.....	.....	34
35	Chrysalis Oil	I	.....	.....	34.5	36.5	.....	.....	.....	35
36	" " , Japanese	I	.851	.....	77 78	.....	199	135.8	.....	36
37	Cocoanut Fat	K	.834	.....	15.7 20.4	24 27	268	8–11	21.2–25.2	37
38	Codliver Oil	E	.....	.....	13.2 24.3	22 25	204–207	164–171	.....	38
39	Coffee Berry Oil	C	.....	.....	34 36	38 40	172–178	88.8–90.4	.....	39
40	Cottonseed Oil	B	.847	.921–.922	30.5 36	35 38 5	204–208	110.9 115 7	28.1–35.2	40

A. Drying Vegetable Oil C. Non-Drying Vegetable Oil E. Liver Oil **I. Animal Oil.** M. Animal Fat O. Solid Vegetable Wax S. Mineral Wax X. Fatty Acid
B. Semi-Drying Vegetable Oil D. Fish Oil **H. Blubber Oil** H Vegetable Fat N. Liquid Wax P. " Animal Wax W. Sulfonated Oil

TABLE XII—PRINCIPAL CONSTANTS OF OILS, FATS AND WAXES—ORIGINAL OIL—*Continued*

			Specific Gravity, H_2O @ 15.5°		Solidifying Point °C.	Melting Point, °C.	Saponification Value	Iodine Value	Acetyl Value	Unsaponifiable Matter, %	Refractive Index, 15.5° C.	
			100° C.	15.5° C.								
41	Cottonseed Stearine	B	.865–.867	.920	16 32.5	26 40	194.6–195.1	88.7–103.8	.....	.....	.....	41
42	Croton Oil	B	.887	.937–.943	−7	.....	192.9–215.6	101.7–122	19.8–32.7	0.55	1.4781 @ 26°	42
43	Curcas Oil	B	.....	.920	−8	−4	193.2	98.3–104.9	8.4–9.8	0.5 –0.6	1.4681–1.487 @ 25°	43
44	Degras (Sod Oil)	P	.....	.921–.984	.....	.....	143–191	68–100	22–48	.....	.....	44
45	Dika Fat	K	.914 @ 40°	.....	27.2 29.4	38.9	244.5	5.2	.....	0.73	.....	45
46	Dolphin Oil { Body	H	.....	.926	+ 5 − 3	.....	197–203	99.5–126.9	.....	2.0	1.4708 }	46
	Dolphin Oil { Jaw	H	.....	.....	+ 5 − 3	.....	270	32.8	.....	2.0	.....	
47	Dogfish Oil	E	.....	.918	.....	.....	169.7	126.4	.....	8.4	.....	47
48	Egg Oil	I	.881	.914	8 10	22 25	184–190	68.5–81.6	.....	.....	1.4713 @ 25°	48
49	Elderberry Oil	C	.....	.907–.917	− 3 − 8	0	196.8–209.3	81.4–110.6	15.5	.....	1.472 @ 26°	49
50	Elazy Oil	C	.....	.916	5 12	.....	155(?)	85.1	.....	2.0	.....	50
51	Fir-seed Oil	A	.....	.921–.933	−18 −30	.....	191.3	118.9–120	.....	.....	.....	51
52	Flax Wax	O	.....	.908	.....	61.5	101.5	9.6	.....	81.3	.....	52
53	Garden Cress Oil	B	.....	.921–.924	− 6 −15	.....	178–186.4	101.7–139.1	.....	.....	.....	53
54	" Rocket Oil	A	.....	.928–.934	−22 −23	.....	191.8	154.9–155.3	.....	.....	.....	54
55	Goose Fat	M	.....	.916–.930	18 20	27.5 34	184–198	58.7– 99.6	.....	.....	.....	55
56	Grapeseed Oil	C	.....	.920–.956	−10 −17	.....	178.3–190	94–142.8	31–144 (?)	.....	1.4713 @ 25°	56
57	Haddock Oil	E	.....	.929–.934	.....	.....	187–193	154–186	.....	1.1–1.3	.....	57
58	Hare Fat	M	.861	.935	17 30	35 46	201	102	.....	.....	.....	58
59	Hazelnut Oil	C	.....	.915–.917	−10 −20	.....	187–197.1	83.2– 90.2	3.2	0.5	.....	59
60	Hempseed Oil	A	.....	.925–.931	−27	.....	190–193.1	140.5–166	7.5	.....	.....	60
61	Herring Oil	D	.....	.918–.939	.....	.....	179–193.7	103.1–142	.....	.....	.....	61
62	Horse Fat	M	.861	.916–.927	20 30	20 43	195–197.1	71.4– 86.3	6.6–13.7	.....	.....	62
63	Horsefoot Oil	I	.....	.920–.927	.....	.....	195–196.8	73.7– 90.3	13.0	.....	.....	63
64	Horse Marrow	M	.....	.920–.922	20 24	35 39	199.7–200	77.6– 80.6	.....	.....	.....	64
65	" Oil	I	.....	.918–.921	.....	.....	195–196	90.1–114.8	.....	0.4–0.7	.....	65
66	Human Fat	M	.....	.918	15	12.5	193–199	57.2– 66.3	.....	0.33	.....	66
67	Jamba Oil	B	.....	.915–.916	−10 −12	.....	172.3–175.3	95.2–102.5	.....	0.5–1.0	.....	67
68	Japan Wax	K	.815	.984–.993	48.5 53	50.4 56	217–237	4.2–15.1	27 –31.2	1.1–1.6	.....	68
69	Japanese Wood (Tung) Oil	A	.....	.933–.942	below −17	.....	155.6–211	149.7–165.7	.....	.....	1.503 @ 19°	69
70	Kapok Oil	B	.....	.923	29.6	.....	196.5–205	117.9–119.4	86	.....	.....	70
71	Koëme Oil	C	.....	.918	7	.....	195.1–197.4	88.3–100.7	26.9	0.9	.....	71
72	Kokum Butter	K	.856	.....	27.5 37.9	36.7 43	187–192	25–34	.....	.....	1.4628 @ 25°	72
73	Lallamantia Oil	A	.....	.959 @ 20°	−35	.....	185	162.1	.....	.....	.....	73
74	Lard Fat	M	.859	.934–.938	27.1 29.9	36 48	195.3–196.6	53–76.9	2.6	0.2–0.4	1.4539 @ 60°	74
75	" Oil	I	.....	.915–.916	− 4 +10	.....	191–196	67–88	.....	.....	.....	75
76	Laurel Fat	K	.880	.933–.953	24 25	32 36	197–210	66–96	.....	.....	1.4643 @ 40°	76
77	Linseed Oil, Boiled	A	.....	.939–.950	below −13	.....	.....	148	.....	.....	.....	77
78	" ", Raw	A	.881	.931–.941	−25	−16 −26	190.0–195.2	170–193	3.98	0.6–1.1	1.4835	78

TABLE XII—PRINCIPAL CONSTANTS OF OILS, FATS AND WAXES—INSOLUBLE FATTY ACIDS—*Continued*

			Specific Gravity		Solidifying Point ° C.	Melting Point ° C.	Saponification Value	Iodine Value	Titer Test ° C.	
			at 100° C. (H_2O @ 15.5°)	at 15.5° C.						
41	Cottonseed Stearine	B	.....	.....	.....	27 30	.....	94.3	24.9–40.8	41
42	Croton Oil	B	.....	.....	18.6 19	.....	201	111.2–111.8	18.6–19	42
43	Curcas Oil	B	.....	.....	.....	24 26	.....	105.1	23.6	43
44	Degras (Sod Oil)	P	.....	.....	.....	24 31	.....	.....	.....	44
45	Dika Fat	K	.....	.....	34.8	.....	.....	.....	.....	45
46	Dolphin Oil { Body	H	.....	.....	.....	.....	.....	.....	.....	46
	Dolphin Oil { Jaw	H	.....	.....	.....	.....	.....	.....	.....	
47	Dogfish Oil	E	.....	.....	.....	.....	.....	.....	.....	47
48	Egg Oil	I	.....	.....	.....	34.5 39	195	72.6–73.3	.....	48
49	Elderberry Oil	C	.....	.....	.....	38 43	204.8	93	.....	49
50	Elazy Oil	C	.....	.....	.....	.....	.....	.....	.....	50
51	Fir-seed Oil	A	.....	.....	10 16	16 19	.....	121.5	.....	51
52	Flax Wax	O	.....	.....	.....	.....	.....	.....	.....	52
53	Garden Cress Oil	B	.....	.....	.....	16 21	186.7–193.4	111.4–144.9	.....	53
54	" Rocket Oil	A	.....	.....	14 16	20 22	.....	157	.....	54
55	Goose Fat	M	.....	.925–.926	31 34	34 49	196.4–202.4	65.1–65.3	.....	55
56	Grapeseed Oil	C	.....	.....	18 20	23 26	187.4	93.7–132.5	.....	56
57	Haddock Oil	E	.....	.....	.....	.....	.....	.....	.....	57
58	Hare Fat	M	.....	.906	36 41	44 50	209	93.3	.....	58
59	Hazelnut Oil	C	.....	.....	9 20	17 25	200.6	87.5 99.6	.....	59
60	Hempseed Oil	A	.....	.....	14 16	17 19	.....	122–141	15.6–16.6	60
61	Herring Oil	D	.....	.....	.....	30 31.5	.....	.....	.....	61
62	Horse Fat	M	.....	.....	37	37.5 39.5	202.7	83.9–87.1	33.6–33.7	62
63	Horsefoot Oil	I	.....	.....	.....	.....	.....	.....	27.1–28.6	63
64	Horse Marrow	M	.....	.918–.929	34 36	42 44	210.8–217.6	71.8–72.2	38.4–38.5	64
65	" Oil	I	.....	.....	.....	.....	.....	.....	.....	65
66	Human Fat	M	.....	.....	30.5	35.5	.....	64	.....	66
67	Jamba Oil	B	.....	.....	11 16	19 21	174	96.2	.....	67
68	Japan Wax	K	.874	.....	53 56.5	54 63	.....	.....	53.8–59.4	68
69	Japanese Wood (Tung) Oil	A	.....	.....	31.2 34	30 43.8	188.8	144.1 159.4	37.1–37.2	69
70	Kapok Oil	B	.....	.916 @ 18°	23 32	29 36	191	108	.....	70
71	Koëme Oil	C	.....	.....	41	44	.....	.....	38.8	71
72	Kokum Butter	K	.....	.....	59.4	60 61	.....	.....	.....	72
73	Lallamantia Oil	A	.....	.....	11	22.2	.....	166	.....	73
74	Lard Fat	M	.837–.840	.....	34 42	35 47	.....	64.2	41.5–42	74
75	" Oil	I	.....	.....	.....	.....	.....	.....	.....	75
76	Laurel Fat	K	.....	.....	.....	.....	.....	82	14.3–15.1	76
77	Linseed Oil, Boiled	A	.....	.....	.....	.....	.....	.....	.....	77
78	" " , Raw	A	.861	.923	13.3 17.5	17 24	196–198.8	178.5–239.8	.....	78

A. Drying Vegetable Oil
B. Semi-Drying Vegetable Oil
C. Non-Drying Vegetable Oil
D. Fish Oil
E. Liver Oil
H. Blubber Oil
I. Animal Oil
K. Vegetable Fat
M. Animal Fat
N. Liquid Wax
O. Solid Vegetable Wax
P. " Animal Wax
S. Mineral Wax
W. Sulfonated Oil
X. Fatty Acid

TABLE XII—PRINCIPAL CONSTANTS OF OILS, FATS AND WAXES—ORIGINAL OIL—*Continued*

			Specific Gravity, H_2O @ 15.5°		Solidifying Point ° C.	Melting Point, ° C.	Saponification Value	Iodine Value	Acetyl Value	Unsaponifiable Matter, %	Refractive Index, 15.5° C.	
			100° C.	15.5° C.								
79	Macassar Fat	K	.....	.924	10	22	215–230	48.3– 69	.....	3	.....	79
80	Madia Oil	A	.....	.926–.929	−10 −22.5	.....	192.8	119–119.5	.....	.....	.....	80
81	Mafura Tallow	K	.....	.....	25 37	35 42	200–221	44.8– 47.5	.....	.....	.....	81
82	Maize (Corn) Oil	B	.871–.876	.921–.927	−10 −20	.....	188–193.4	111.2–128	.....	1.3–2.3	1.4768	82
83	Malabar Tallow	K	.890 (H_2O @ 100)	.915	30.5	30 42	188–193	38–40	.....	.....	.....	83
84	Manihot Oil	A	.....	.926	.....	below −17	188.6	137	.....	.....	.....	84
85	Menhaden Oil	D	.877	.927–.933	−4	.....	189–193	139–172	.....	0.6 1.6	.....	85
86	Mowrah Seed Oil	K	.894–.898	.917	17.2 22	23 31	187.4–194	53.4– 67.8	.....	.....	.....	86
87	Mustard Oil, Black	B	(H_2O @ 100°)	.916–.921	17.5	.....	172–180	96–122.3	60	.....	1.4672	87
88	" ", Hedge	B	.....	.917	8	.....	174	105	.....	.....	.....	88
89	" ", White	B	.....	.914–.916	−16	.....	170.3–174.6	92–103	.....	.....	1.4750	89
90	Mutton Tallow	M	.858–.860	.937–.953	32 41	44 49	192–195	32.7– 46.7	.....	.....	1.4501 @ 60°	90
91	Myrtle Wax	K	.875–.878	.995	39 45	40 48	205.7–217	1.95–3.9	.....	0.5	1.4363 @ 80°	91
92	Neatsfoot Oil	I	.862	.914–.917	− 4 +10	.....	194.3–199	66–76	22	0.1–0.7	1.4681 @ 20°	92
93	Niger Seed Oil	A	.873	.925–.927	−9	.....	189–193	133	.....	.....	.....	93
94	Nutmeg Butter	K	.898	.945–.996	39 44	38.5 51	153.5–191.4	40–86	.....	.....	1.4704 @ 40°	94
95	Nux Vomica Fat	K	.864 (H_2O @ 100)	.883 @ 20°	.....	28 31	166–170.6	69–79	11.6–42	12 –17	.....	95
96	Oleic Acid, Pure	X	.....	.898	4	14	198.9	90.07	.....	.....	.....	96
97	Oleomargarine	M	.858–.863	.924–.930	18 38	34 40	193.7–203	35–60.9	.....	.....	.....	97
98	Olive Oil	C	.....	.914–.920	− 6 +10	.....	185–203	77.3– 93.5	10.64	0.5–1.4	1.4698–1.4715	98
99	" Kernel Oil	C	.....	.918–.919	.....	.....	181.2–183.8	87.0–87.8	22.5	.....	1.4673–1.4688 @ 25°	99
100	Ostrich Oil	I	.....	.926	2	8	211	71.1	.....	.....	.....	100
101	Owala Oil	C	.864	.920 @ 25°	4 20.6	22 24.5	167.6–186	94.3–99.3	.....	2.5–2.7	1.4654 @ 40°	101
102	Palm Oil	K	.851	.921–.925	31 39	27 42.5	196.3–205.1	53–57.4	18	.....	1.4510 @ 60°	102
103	" Nut Oil	K	.873	.952	23 24	23 30	242–250	10.3–17.5	1.9–8.4	.....	1.4431 @ 60°	103
104	Paraffine Wax	S	.748–.757	.867–.911	44 58.5	38 82	.....	4	.....	.....	.....	104
105	Peach Kernel Oil	C	.....	.920	below −20	.....	189.1–192.5	92.5–110.1	6.4	.....	.....	105
106	Perilla Oil	A	.....	.931 @ 20°	.....	.....	189.6	206.1	.....	.....	.....	106
107	Persimmon Seed Oil	B	.....	.924	−11	−6	188	116.8	.....	.....	.....	107
108	Pistachio Nut Oil	C	.....	.919	− 8 −10	.....	191–191.6	86.8– 87.8	.....	.....	.....	108
109	Plum Kernel Oil	C	.....	.916–.920	− 5 −10	.....	189.1–191.6	91.2–100.4	.....	.....	.....	109
110	Poppy Seed Oil	A	.....	.924–.927	−18	.....	190–197.7	134–142	13.1	.....	1.4773	110
111	Porpoise Oil	H	.871	.926	−16	.....	195–257	88–119	.....	.....	.....	111
112	Porpoise Jaw Oil { Skimmed / Not Skimmed	H / H	..... /	.926 /	..... /	..... /	254–272 / 143.9	21.5–49.6 / 16.8	..... /	..... / 16.4	..... /	112
113	Pumpkin Seed Oil	B	.....	.920–.925	−16	.....	188.4–190.2	120–130	.....	.....	.....	113
114	Quince Oil	C	.....	.922	−11 −13	.....	181.7–187.7	113–120.2	.....	.....	1.4729	114
115	Rabbit Fat	M	.861	.934–.939	11 30	35 46	199.3–202.6	67.6– 99.8	.....	.....	.....	115
116	Radish Seed Oil	B	.....	.916–.917	−10 −17.5	.....	173.8–179.4	92.8–112.4	.....	.....	.....	116

TABLE XII—PRINCIPAL CONSTANTS OF OILS, FATS AND WAXES—INSOLUBLE FATTY ACIDS—*Continued*

			Specific Gravity		Solidifying Point ° C.	Melting Point ° C.	Saponification Value	Iodine Value	Titer Test ° C.	
			at 100° C. (H_2O @ 15.5°)	at 15.5° C.						
79	Macassar Fat	K	.....	.....	.....	54 55	191–192	49.7–50.7	51.6–53.2	79
80	Madia Oil	A	.....	.....	20 22	23 26	.....	120.7	.....	80
81	Mafura Tallow	K	.....	.....	44 49.5	51 55	197 *	46.9–48.7	44–48	81
82	Maize (Corn) Oil	B	.853	.....	14 16	18 21.6	198.4	113–125	19	82
83	Malabar Tallow	K	.....	.....	54.8	56.6	.....	.....	.....	83
84	Manihot Oil	A	.....	.898	20.5	23.5	200	143.1	.....	84
85	Menhaden Oil	D	.....	.....	.....	.....	.....	.....	.....	85
86	Mowrah Seed Oil	K	.....	.....	38	39.5	.....	56.7	38.3–38.5	86
87	Mustard Oil, Black	B	.....	.....	15.5	15 17	179–187	109.6–126	.....	87
88	" ", Hedge	B	.....	.....	.....	.....	.....	.....	.....	88
89	" ", White	B	.....	.....	.....	15 16	185.8	94.7 –106.7	.....	89
90	Mutton Tallow	M	.....	.....	39 41	46 54	210	34.8	43–46	90
91	Myrtle Wax	K	.....	.....	46	47.5 48.5	.....	.....	.....	91
92	Neatsfoot Oil	I	.871–.875	.....	26.1	28.5 30	200.6–206.3	62–77	16–26.5	92
93	Niger Seed Oil	A	.889 (H_2O @ 100°)	.....	.....	.....	.....	147.5	.....	93
94	Nutmeg Butter	K	.....	.....	40 45	42.5 49	.....	31.6	35.5–36	94
95	Nux Vomica Fat	K	.....	.....	.....	.....	.....	.....	.....	95
96	Oleic Acid, Pure	X	.....	.....	.....	.....	.....	.....	.....	96
97	Oleomargarine	M	.....	.....	39.8	42	203–211	.....	40	97
98	Olive Oil	C	.843	.....	21 24.6	19 29.3	193	86.1–90.2	.....	98
99	" Kernel Oil	C	.....	.....	.....	.....	.....	.....	.....	99
100	Ostrich Oil	I	.....	.....	.....	35.5	.....	.....	.....	100
101	Owala Oil	C	.....	.....	52.1	52.4 53.9	185.7	.....	.....	101
102	Palm Oil	K	.837	.....	35.8 46.7	47.8 50	204–207.3	53.3	35.8–45.5	102
103	" Nut Oil	K	.....	.....	.....	20.7 28.5	251–265	12.1	20–25.5	103
104	Paraffine Wax	S	.....	.....	.....	.....	.....	.....	.....	104
105	Peach Kernel Oil	C	.....	.....	.....	3 18.9	205–210	94.1–101.9	13–13.5	105
106	Perilla Oil	A	.....	.....	.....	—5	197.7	210.6	.....	106
107	Persimmon Seed Oil	B	.....	.903	.....	20.2	192.7	134–135	20.2	107
108	Pistachio Nut Oil	C	.....	.....	13 14	17 20	.....	88.9–96.2	.....	108
109	Plum Kernel Oil	C	.....	.....	12 15	12 22	200.5	95.7–104.2	.....	109
110	Poppy Seed Oil	A	.889 (H_2O @ 100°)	.....	16.5	20.2 20.5	199	139	.....	110
111	Porpoise Oil	H	.....	.....	.....	.....	.....	.....	.....	111
112	Porpoise Jaw Oil { Skimmed	H	.....	.....	.....	.....	.....	.....	.....	112
	{ Not Skimmed	H	.....	.....	.....	.....	.....	.....	.....	
113	Pumpkin Seed Oil	B	.....	.....	24.5	26.5 29.8	.....	.....	.....	113
114	Quince Oil	C	.....	.....	26 27	33 34	.....	124.6	.....	114
115	Rabbit Fat	M	.....	.925–.926	35 41	39 50	209.5–218	64.4–101.1	.....	115
116	Radish Seed Oil	B	.....	.....	13 15	20	189.5	97.1–115.3	.....	116

A. Drying Vegetable Oil C. Non-Drying Vegetable Oil E. Liver Oil I. Animal Oil M. Animal Fat O. Solid Vegetable Wax S. Mineral Wax X. Fatty Acid
B. Semi-Drying Vegetable Oil D. Fish Oil H. Blubber Oil K. Vegetable Fat N. Liquid Wax P. " Animal Wax W. Sulfonated Oil

TABLE XII—PRINCIPAL CONSTANTS OF OILS, FATS AND WAXES—ORIGINAL OIL—*Continued*

			Specific Gravity, H_2O @15.5°		Solidifying Point °C.	Melting Point °C.	Saponification Value	Iodine Value	Acetyl Value	Unsaponifiable Matter, %	Refractive Index, 15.5° C.	
			100° C.	15.5° C.								
117	Rape (Colza) Oil	B	.863	.913-.918	+10 −10	.....	167-179.1	94.1-104.8	14.7-23.1	0.5-1.0	1.4720-1.4757	117
118	Ravison Oil	B	.....	.915-.922	−8	.....	172.9-179.3	101.4-121.7	.....	1.4-1.7	.....	118
119	Red Oil	X	.848	.899-.908	.....	.....	.....	80-110	.....	1.0-10.3	1.4638	119
120	Rice Oil	C	.890 (H_2O @ 100)	.923	2.1	.....	193.2-193.5	91.6-106.5	.....	.....	.....	120
121	Rosin Oil		.....	.960-1.012	.....	.....	.....	.....	.....	.....	.....	121
122	Saffron Oil	A	.....	.925-.928	below −13	.....	186.6-194.4	130-150	12.8-16.1	.....	1.477 @ 16°	122
123	Sawarri Fat	K	.....	.808 @ 40°	23.3 29	29.5 35.5	199.5	49.5	14.03	.....	.....	123
124	Salmon Oil	D	.....	.926	.....	.....	182.8	161.4	.....	.....	.....	124
125	Sanguinella Oil	C	.....	.921	−15	.....	192	100.8	.....	.....	.....	125
126	Sardine Oil	D	.....	.933	.....	20 22	185.5	161-192	.....	0.5-1.01	.....	126
127	" " Japanese	D	.....	.916-.935	.....	.....	189.8-196.2	121.5-187	13.0	0.6-1.44	1.4802 @ 20°	127
128	Seal Oil	H	.873	.924-.929	− 2 − 3	.....	178-196	127-193.3	16.5	0.4-1.4	1.4762 @ 20°	128
129	Senega Root Oil	C	.....	.962 @ 18°	.....	.....	193.8	78.4-.81.8	34.46	12.8	.....	129
130	Sesame Oil	B	.868	.920-.926	− 4 − 6	.....	187.6-194.6	103-115	11.5	0.9-1.3	1.4748-1.4762	130
131	Shark Oil	E	.....	.910-.918	.....	.....	146-163	90-136	11.9	10-22	.....	131
132	Shea Butter	K	.859	.917	17 18	23 28	171.8-192.3	54-67.2	.....	3.6-9.7	.....	132
133	Sheepsfoot Oil	I	.....	.917-.918	0 1.5	.....	194.8	74-74.4	.....	.....	.....	133
134	Skunk Oil	M	.....	.917	.....	.....	206	.....	.....	.....	.....	134
135	Soja Bean Oil	B	.....	.924-.927	8 15	.....	190.6-192.9	121.3-124	.....	0.22	1.4777	135
136	Sperm Oil	N	.830	.844-.881	.....	.....	122-150.3	81.3- 90.1	4.5-6.4	37-44	1.4646-1.4655 @ 20°	136
137	Spermaceti Oil	P	.808-.816	.905-.960	41 48	41 49	120.6-134.6	3.8	2.6	51-54	.....	137
138	Sterculia Oil	C	.....	.926	.....	.....	187.9	76.6	.....	1.7	1.4654 @ 40°	138
139	Sturgeon Oil	D	.....	.924	.....	.....	186.3	125.3	.....	1.78	.....	139
140	Sunflower Oil	A	.....	.924-.926	−16 −18.5	.....	188-194	120-135	.....	0.3-0.7	.....	140
141	Tallow Oil	I	.794	.916	0 6	.....	196.5	55.8-56.7	.....	.....	.....	141
142	Tallowseed Oil	A	.874	.940	.....	.....	203.8-210.4	145.6-160.7	.....	.....	1.4825 @ 23½°	142
143	Tea Seed Oil	C	.....	.917-.927	− 5 −12	.....	188.3-195.5	88-90.5	.....	.....	.....	143
144	Tobacco Seed Oil	A	.....	.923	−25	.....	190	118.5	.....	.....	.....	144
145	Tsubaki Oil	C	.....	.916-.917	.....	−15	180.9-192.6	80.1-81.3	.....	.....	1.468-1.469 @ 20°	145
146	Turkey Red Oil	W	.....	.....	.....	.....	.....	.....	over 125	0.15±	.....	146
147	Turtle Oil	H	.....	.919 @ 25°	10 19	23 27	209-211	111-112	.....	.....	1.4677 @ 30°	147
148	Ucuhuba Fat	K	.....	.....	32.5	39 43	219-220	9.5	.....	.....	.....	148
149	Ungnadia Oil	C	.854	.912	−12	.....	191-192	81.5-82	.....	.....	.....	149
150	Vegetable Tallow	K	.860	.915-.918	24.2 37.7	35 53	179-231	19-38	.....	.....	.....	150
151	Walnut Oil	A	.....	.925-.926	−27.5	.....	188.7-196.6	143-152	7.6	.....	1.4804	151
152	Whale Oil	H	.872	.917-.927	−2	.....	187.9-199.2	110.1-146.6	.....	0.6-3.7	1.4762 @ 20°	152
153	Wheat Oil	B	.....	.925-.937	15	.....	182.8-190.3	115-115.6	.....	.....	1.48325 @ 20°	153
154	Wool Oil	P	.901	.943-.947	30 30.2	31 42.5	98.3-102.4	17.1- 28.9	23.3	43-52	1.4781-1.4822 @ 20°	154

TABLE XII—PRINCIPAL CONSTANTS OF OILS, FATS AND WAXES—INSOLUBLE FATTY ACIDS—*Continued*

			Specific Gravity		Solidifying Point ° C.	Melting Point ° C.	Saponification Value	Iodine Value	Titer Test ° C.	
			at 100° C. (H_2O @ 15.5°)	at 15.5° C.						
117	Rape (Colza) Oil	B	.844	.....	16 18	16 20	185	96–105.6	11.7–13.6	117
118	Ravison Oil	B	.880	.....	.....	.....	.....	124–126.1	.....	118
119	Red Oil	X	.876	.....	.....	.....	.....	.....	.....	119
120	Rice Oil	C	.....	.....	28 29	31 36	97.4–109	.....	.....	120
121	Rosin Oil	..	.....	.....	.....	.....	.....	.....	.....	121
122	Saffron Oil	A	.....	.914	.....	16 16.5	199	132.5–159	16	122
123	Sawarri Fat	K	.....	.....	46 47	43.3 50	.....	51.5	46–47	123
124	Salmon Oil	D	.....	.....	.....	.....	.....	.....	.....	124
125	Sanguinella Oil	C	.....	.....	29 31	34 37	195.1	102.8	.....	125
126	Sardine Oil	D	.....	.....	.....	.....	.....	.....	.....	126
127	" , Japanese	D	.....	.....	35.4 36.2	.....	.....	.....	28.2	127
128	Seal Oil	H	.....	.915–.917	.....	14 33	190.4–198	186.5–201.8	15.5–17	128
129	Senega Root Oil	C	.....	.....	.....	.....	.....	.....	.....	129
130	Sesame Oil	B	.....	.....	18.5 28.5	21 32	199.3–201.6	108.9–112	21.2–23.8	130
131	Shark Oil	E	.....	.....	.....	.....	.....	.....	.....	131
132	Shea Butter	K	.....	.....	38 52	39.5 56.5	.....	56–57	48.6–53.8	132
133	Sheepsfoot Oil	I	.....	.....	.....	.....	.....	.....	20–21.1	133
134	Skunk Oil	M	.....	.....	.....	.....	.....	.....	.....	134
135	Soja Bean Oil	B	.....	.....	24 25	27 29	.....	115–122	.....	135
136	Sperm Oil	N	.....	.899	16.1	13.3 21.4	.....	83.2–88.1	11.1–11.9	136
137	Spermaceti Oil	P	.....	.....	.....	.....	.....	.....	.....	137
138	Sterculia Oil	C	.....	.....	.....	46.5	.....	58	43	138
139	Sturgeon Oil	D	.....	.....	.....	.....	.....	.....	.....	139
140	Sunflower Oil	A	.....	.....	17 18	17 24	201.5	124–134	.....	140
141	Tallow Oil	I	.....	.....	.....	.....	.....	54.6–57	34.5–37.5	141
142	Tallowseed Oil	A	.....	.....	.....	14.5	206.3–214.2	161.9–191.1	12.2	142
143	Tea Seed Oil	C	.....	.....	.....	10 11	195	90.8	.....	143
144	Tobacco Seed Oil	A	.....	.....	.....	.....	.....	.....	.....	144
145	Tsubaki Oil	C	.840	.....	.....	22	197	83.7	.....	145
146	Turkey Red Oil	W	.....	.945	.....	.....	189	82	.....	146
147	Turtle Oil	H	.....	.....	28.2	30.2	.....	119	.....	147
148	Ucuhuba Fat	K	.....	.....	.....	42.5 46	.....	.....	.....	148
149	Ungnadia Oil	C	.....	.....	10	19	.....	86–87	.....	149
150	Vegetable Tallow	K	.....	.....	.....	47 57	182–208	29.2–54.8	40–56.4	150
151	Walnut Oil	A	.....	.....	16	15 20	.....	150	.....	151
152	Whale Oil	H	.892 (H_2O @ 100°)	.....	.....	14 27	.....	130–132	22.9–23.9	152
153	Wheat Oil	B	.....	.....	29.7	39.5	.....	123.3	.....	153
154	Wool Oil	P	.....	.....	40	41.8	.....	17	.....	154

A. Drying Vegetable Oil
B. Semi-Drying Vegetable Oil
C. Non-Drying Vegetable Oil
D. Fish Oil
E. Liver Oil
H. Blubber Oil
I. Animal Oil
K. Vegetable Fat
M. Animal Fat
N. Liquid Wax
O. Solid Vegetable Wax
P. " Animal Wax
S. Mineral Wax
W. Sulfonated Oil
X. Fatty Acid

NOTES.—(1) The correctness of the instrument should be checked by means of the quartz plate which accompanies it, using monobromonaphthalene. It may also be checked with distilled water, the index of refraction of which at 20° C. is 1.3330. Apply to all readings any correction found in standardization.

(2) Refractive index varies inversely with temperature, increasing as temperature falls and *vice versa*. Temperature correction may be made as follows:

Let	R_1 = reading at t_1,
and	R_2 = reading at t_2;
then	$R_1 = R_2 + 0.00038\ (t_2 - t_1)$.

The decimal in the formula represents the change in refractive index for each degree C.

BY ZEISS BUTYRO-REFRACTOMETER.—Place 2 or 3 drops of the filtered fat on the surface of the lower prisms. Close the prisms and adjust the mirror until it gives the sharpest reading. If the reading is indistinct after running water at constant temperature through the instrument for some time, the fat is unevenly distributed on the surfaces of the prisms. The instrument should be carefully adjusted by means of a standard fluid supplied with it and the temperature kept constant while all readings are being taken. Convert degrees butyro to refractive indices from the following table:

TABLE XIII—BUTYRO-REFRACTOMETER READINGS AND INDICES OF REFRACTION

Reading	Index	Reading	Index	Reading	Index	Reading	Index
40.0°	1.4524	50.0°	1.4593	60.0°	1.4659	70.0°	1.4723
40.5	1.4527	50.5	1.4596	60.5	1.4662	70.5	1.4726
41.0	1.4531	51.0	1.4600	61.0	1.4665	71.0	1.4729
41.5	1.4534	51.5	1.4603	61.5	1.4668	71.5	1.4732
42.0	1.4538	52.0	1.4607	62.0	1.4672	72.0	1.4735
42.5	1.4541	52.5	1.4610	62.5	1.4675	72.5	1.4738
43.0	1.4545	53.0	1.4613	63.0	1.4678	73.0	1.4741
43.5	1.4548	53.5	1.4616	63.5	1.4681	73.5	1.4744
44.0	1.4552	54.0	1.4619	64.0	1.4685	74.0	1.4747
44.5	1.4555	54.5	1.4623	64.5	1.4688	74.5	1.4750
45.0	1.4558	55.0	1.4626	65.0	1.4691	75.0	1.4753
45.5	1.4562	55.5	1.4629	65.5	1.4694	75.5	1.4756
46.0	1.4565	56.0	1.4633	66.0	1.4697	76.0	1.4759
46.5	1.4569	56.5	1.4636	66.5	1.4700	76.5	1.4762
47.0	1.4572	57.0	1.4639	67.0	1.4704	77.0	1.4765
47.5	1.4576	57.5	1.4642	67.5	1.4707	77.5	1.4768
48.0	1.4579	58.0	1.4646	68.0	1.4710	78.0	1.4771
48.5	1.4583	58.5	1.4649	68.5	1.4713	78.5	1.4774
49.0	1.4586	59.0	1.4652	69.0	1.4717	79.0	1.4777
49.5	1.4590	59.5	1.4656	69.5	1.4720	79.5	1.4780

Saponification Number (Koettstorfer Number).—Saponify about 5 grams (accurately weighed) by boiling under a reflux condenser for 1 hour with 50 cc. of 0.5 N alcoholic KOH in a 250–300-cc. Erlenmeyer flask. Run a blank on 50 cc. of the 0.5 N alcoholic KOH (measured with the same pipette) under the same conditions. Cool and titrate with 0.5 N HCl and phenolphthalein. Always make duplicate determinations. Subtract the number of cc. of acid used to neutralize the excess of alkali after saponification from the number of cc. required by the blank. Multiply the difference by 28.05 and divide by the weight of sample to obtain the saponification number, which represents milligrams of KOH consumed by 1 gram of oil.

Alcoholic KOH Solution.—Dissolve 30 grams of pure KOH in 1 liter of 95% alcohol by volume, which has been redistilled

from NaOH, over which it has been standing for some time, or boiled for a short time under a reflux condenser with stick NaOH and then distilled. Mix thoroughly and let stand until all carbonate has settled out. Pour off the clear solution for use.

Unsaponifiable Matter.—See page 340.

Iodine Number.—Determine the iodine number by the Wijs method. Weigh 0.10–0.50 gram of oil (depending upon its iodine number) into a wide-mouthed, glass-stoppered bottle. (For drying oils, such as linseed, use between 0.15 and 0.20 gram. Also see note.) Add 15 cc. of $CHCl_3$ or CCl_4. Then add from a pipette 25 cc. of Wijs solution.* Moisten the stopper with 15% KI solution but do not use sufficient to run down inside the bottle. Let stand 1 hour; add 20 cc. of 15% KI solution and 100 cc. of recently boiled and cooled water and titrate immediately with 0.1 N thiosulfate solution, running in rapidly at first until the color begins to fade, then adding starch solution and titrating more slowly until the blue color disappears. The bottle should be stoppered and shaken violently during titration to make sure that all excess of iodine is removed from the $CHCl_3$ or CCl_4. Run 2 blanks with each determination, following exactly the same procedure but omitting the oil. Take care to have the temperature the same at the end of the determination as at the beginning.

Subtract the number of cc. of thiosulfate required in the oil titration from the average number of cc. required by the 2 blanks, multiply by 1.269 and divide by the weight of oil taken. The iodine number represents the number of centigrams of iodine absorbed by 1 gram of oil, *i.e.*, the percentage of iodine absorbed.

Wijs Solution.—Dissolve 13.0 grams of resublimed iodine in 1 liter of pure glacial acetic acid. Titrate a portion with 0.1 N thiosulfate. Set aside about 25 cc. Into the remainder pass washed and dried chlorine gas until the original thiosulfate titration† is just doubled. (It is very necessary that the

* The excess of iodine should be 50–60% of the quantity added, *i.e.*, 100–150% of the quantity absorbed. If such is not the case, repeat the determination, using a smaller or larger amount of the sample.

† Before titration of the chlorinated liquid add 20 cc. of 15% KI solution and 100 cc. of water.

chlorine gas be passed through conc. H_2SO_4 to dry it, as moisture spoils the solution.) Then add the small portion of the original solution to neutralize any free chlorine. Preserve in amber-colored glass-stoppered bottles and mark the date on the bottles. Wijs solution deteriorates on standing and should not be used after it is more than 1 month old.

NOTE.—*Determination on Tung Oil.*—Tung oil shows an erratic behavior with most iodine reagents but the Wijs solution gives reliable results if the following precautions are observed: Weigh out between 0.10 and 0.20 gram and use an excess of 52–58% of Wijs solution. Let the absorption run for 1 hour at 20–25° C.

Acid Number (Free Fatty Acids).—Weigh 20 grams of the sample (see note 1) into a 300-cc. Erlenmeyer flask. Add 50 cc. of 95% alcohol previously neutralized with 0.1 N NaOH and phenolphthalein. Heat to boiling on the steam bath, agitate the flask thoroughly, and titrate with 0.1 N KOH (or NaOH), shaking thoroughly, until the pink color persists. The *acid number* is expressed as milligrams of KOH required per 1 gram of oil.

CALCULATION.—1 cc. 0.1 N KOH = 5.61 mg. KOH.

In case the *percentage of fatty acids* is desired, use the following factor: 1 cc. 0.1 N KOH = 0.02823 gram oleic acid.

It will be noted that the percentage of oleic acid × 1.99 = acid number.

NOTES.—(1) In the case of dark-colored, high-acid fats use a smaller sample or titrate with 0.5 N caustic. If the titration requires over 15 cc. of alkali, either reduce the amount of sample taken for the test or titrate with 0.1 N *alcoholic* KOH (or NaOH).

(2) For accurate results the alcohol should be freshly distilled from NaOH and give a sharp end-point with phenolphthalein. For routine tests methyl alcohol or No. 30 special denatured alcohol of about 95% strength may be used.

(3) The Bureau of Standards recommends dissolving the oil in 50 cc. of a mixture of equal volumes of ethyl alcohol and C. P. benzene, previously neutralized to a faint pink with phenolphthalein. The titration may be made at once without heating and a sharper end-point is obtained. (See *J. Ind. Eng. Chem.*, **14,** 57 (1922)).

Melting Point.—Determine the melting point by the closed capillary tube method. Draw the melted sample into a thin-walled capillary tube of 1 mm. inside diameter. Use a column

of fat 1–2 cm. long, according to the length of the thermometer bulb. Seal one end of the tube and cool on ice for 12–15 hours. Attach the capillary tube with a rubber elastic to the bulb of an accurate thermometer;* immerse in a large test-tube of water surrounded by a beaker of water, and heat very slowly, about 1° per minute. An apparatus similar to that shown in Fig. 17 may be used, agitating the water with an air current. Record the temperature at which the fat becomes uniformly transparent as its melting point. The fat becomes opalescent and usually appears clear at the top, bottom and sides before becoming clear at the center. This generally occurs a fraction of a degree before it becomes uniformly clear.

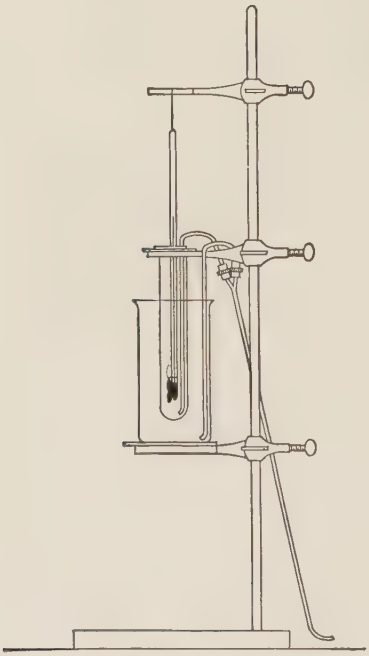


Fig. 17.—Melting Point Apparatus.

Notes.—(1) The above method is not applicable to emulsified fats or oils, such as butter and oleomargarine. Not only the amount of water present but its state of subdivision and distribution in a fat or oil influences the melting point and causes it to vary widely in different samples.

(2) In legal cases and cases of dispute use the Wiley method as described in Association of Official Agricultural Chemists: "Methods of Analysis," 284 (1925).

Titer Test.—Either of the following methods may be used. Method *B* is much quicker and the saving in time will generally more than offset the extra cost of chemicals.

(*A*) Alcoholic or Aqueous NaOH Method.—(1) *Standard Thermometer.*—The thermometer must have a zero mark, 0.1° graduations between 10 and 60° C., and auxiliary reservoirs at the upper end and between the 0 and 10° marks. The cavity in the capillary tube between the 0 and 10° marks must be at least

* The official method of the A. O. A. C. requires the thermometer to be graduated to 0.2° C. Results should be reported to the nearest 0.5° C.

1 cm. below the 10° mark, which must be 3–4 cm. above the bulb, the total length of the thermometer being about 38 cm. The bulb should be about 3 cm. long and 6 mm. in diameter. The stem of the thermometer should be 6 mm. in diameter and made of the best thermometer tubing, thoroughly annealed, with the scale etched on the stem, graduations clear cut and distinct. It must be certified by the U. S. Bureau of Standards.

(2) *Determination.*—Saponify 75 grams of the sample in a metal dish with 60 cc. of 30% NaOH solution (36° Bé.) and 75 cc. of 95% alcohol* by volume or 120 cc. of water. Evaporate to dryness over a very low flame or on an iron or asbestos plate, stirring constantly. Dissolve the dry soap in 1 liter of boiling water and, if alcohol has been used, boil for 40 minutes to remove it, adding sufficient water to replace that lost in boiling. Liberate the fatty acids by adding 100 cc. of dil. H_2SO_4 (1:3) and boil until they form a clear, transparent layer. Wash with boiling water until free from H_2SO_4, collect in a small beaker and place on the steam bath until the water has settled and the fatty acids are clear; then decant into a dry beaker, filter while hot and dry for 20 minutes at 100° C. If preferred, the fatty acids may be dried by heating rapidly in a beaker to 130° C. while stirring.

Test the fatty acids for complete saponification as follows: Place 3 cc. in a test-tube and add 15 cc. of 95% alcohol. Bring the mixture to boiling and add an equal volume of dil. NH_4OH (1:2). A clear solution should result.

When dried, cool the fatty acids to 15–20° C. above the expected titer and transfer to a titer-tube, 25 by 100 mm. (1 by 4 inches) and made of glass about 1 mm. in thickness. Place in a 16-ounce wide-mouthed bottle of clear glass, 70 by 150 mm. (2.8 by 6 inches) fitted with a perforated cork so as to hold the tube rigidly when in position. Suspend the standard thermometer so that it can be used as a stirrer, and stir the mass slowly (about 100 r. p. m.) until the mercury remains stationary for 30 seconds. Then let the thermometer hang quietly, with the bulb in the center of the mass, and observe the rise of the mercury column. Report the highest point to which it rises as the titer of the fatty acids. The titer test must be made at about

* Methyl alcohol or No. 30 specially denatured alcohol may also be used.

20° C. for all fats having a titer above 30° C. and at 10° C. below the titer for all others.

(*B*) GLYCEROL-KOH METHOD.—Heat 75 cc. of glycerol-KOH solution (25 grams of KOH in 100 cc. of high-test glycerol*) to 150° C. in an 800-cc. beaker; then add 50 cc. of the oil or melted fat, previously filtered if necessary to remove foreign substances. Saponification often takes place almost immediately, but heating with frequent stirring should be continued for 15 minutes, avoiding a temperature above 150° C. When saponification is complete, as indicated by a perfectly homogeneous solution, pour the soap solution into an 800-cc. casserole containing about 500 cc. of nearly boiling water, add carefully 50 cc. of dil. H_2SO_4 (1:3) and heat the solution, with frequent stirring, until the layer of fatty acids separates out perfectly clear. Transfer the fatty acids to a tall separatory funnel, wash three or four times with boiling water to remove all mineral acids, draw the fatty acids off into a small beaker, and let stand on the steam bath until the water has settled out and the acids are clear. Filter into a dry beaker and heat as rapidly as possible to 150° C. on a thin asbestos plate, stirring continually with the thermometer; transfer to the titer-tube, fill it to within 2.5 cm. of the top and determine the titer as directed above.

Cloud Test.—See page 328.

Moisture and Volatile Matter.—The most accurate method for determining moisture and volatile matter in fats and fatty oils is by drying in a vacuum oven, and a small oven is preferable in order to obtain uniform temperature at all points. Weigh out accurately 4.8–5.2 grams of the prepared sample into a shallow glass dish, preferably with a lip, approximately 6–7 cm. in diameter and 4 cm. deep, and dry to constant weight *in vacuo* at a uniform temperature not less than 15° C. nor more than 20° C. *above* the boiling point of water at the working pressure, which must not exceed 100 mm. of mercury (see note 3). Constant weight is attained when successive dryings for 1-hour periods show an additional loss of not more than 0.05%. Report the percentage loss in weight as Moisture and Volatile Matter.

NOTES.—(1) Results comparable to the vacuum oven method can be obtained on most fats and oils by drying 5-gram portions to constant

* Dynamite glycerine or U. S. P.

weight in a well-constructed and well-ventilated air oven at a temperature of 105–110° C. The thermometer bulb should be close to the sample. This method, however, cannot be considered even approximately accurate in the case of drying and semidrying oils (linseed, soya bean, cottonseed, maize oil, etc.) and those of the cocoanut oil group.

(2) In the case of fats of the cocoanut group containing more than 1% free acid, even the vacuum method is not accurate on account of the volatility of the acids. The following method gives more accurate results on oils of this class and also, if carefully carried out, is a satisfactory method for routine control work on all kinds of fatty oils:

Weigh out 5–25 grams of the prepared sample into a glass beaker or casserole and heat on a heavy asbestos board over a burner or hot plate, taking care that the temperature of the sample does not go above 130° C. at any time. During the heating rotate the vessel gently on the board by hand to avoid sputtering. The proper length of time of heating is judged by the absence of rising bubbles of steam or foam. Avoid overheating of the sample as indicated by smoking or darkening. Cool in a desiccator and weigh. (There is a considerable personal factor in this method until the operator has become familiar with it.)

(3) The following table gives the temperatures to be used with various pressures in the vacuum oven method:

Pressure, Mm. of Hg.	Boiling Point of Water, °C.	Proper Temperature of Oven, °C.
100	52	67–72
90	50	65–70
80	47	62–67
70	45	60–65
60	42	57–62
50	38	53–58
40	34	49–54

Insoluble Impurities.—Dissolve the residue from the Moisture and Volatile Matter by heating on the steam bath with 50 cc. of kerosene. Filter through a Gooch crucible which has been dried and weighed with its asbestos mat, wash the insoluble matter 5 times with 10-cc. portions of hot kerosene and finally wash the residual kerosene out thoroughly with petroleum ether. Dry the crucible and contents to constant weight and report results as Insoluble Impurities.

NOTE.—A tared filter paper may be used in place of the Gooch crucible but it must be very carefully washed, especially around the edges, to remove the last traces of fat.

Soluble Mineral Matter.—Place the combined kerosene filtrate and washings from the Insoluble Impurities in a platinum dish. Place in this a quantitative filter paper folded in the form of a cone with the apex up. Light the apex of the cone and let the bulk of the kerosene burn off quietly. Ash the residue in a muffle to constant weight, taking care that the decomposition of $CaCO_3$ and $MgCO_3$ is complete, and report the result as Soluble Mineral Matter. When the amount is more than 0.1%, multiply the percentage by 10 and add this amount to the percentage of Free Fatty Acids as previously determined.

NOTES.—(1) Soluble mineral matter represents mineral matter combined with fatty acid in the form of soaps. These generally consist mostly of lime soap, in which the ratio of CaO to fatty acid is 1:10.

(2) When the ash contains phosphates, as in the case of bone greases, the factor 10 cannot be applied, but the actual percentage of bases must be determined and the factor 10 applied to them.

REFERENCE.—Association of Official Agricultural Chemists: "Methods of Analysis," 281 (1925); *J. Ind. Eng. Chem.*, "Standard Methods for Sampling and Analysis of Commercial Fats and Oils," **11,** 1161 (1919).

SPECIAL TESTS

Cholesterol and Phytosterol (in Mixtures of Animal and Vegetable Fats).—Introduce 200–300 grams (accurately weighed, if a determination of Unsaponifiable Matter is desired) of melted fat into a flat-bottomed liter flask. Close the neck of the flask with a 3-hole stopper and insert through these holes: (1) a reflux condenser; (2) a right-angled glass tube, one arm of which reaches to a point 6 mm. above the surface of the melted fat, the other being closed a short distance from the flask by means of a short piece of rubber tubing and a pinch-cock; (3) a glass tube bent so that one arm reaches down to the bottom of the flask and the other serves as a delivery tube for a 700-cc. round-bottomed flask containing 500 cc. of 95% alcohol by volume.

Place the flasks, containing the melted fat and alcohol, respectively, on a steam bath and heat so that the alcohol vapor passes through the melted fat in the liter flask and is condensed in the reflux condenser, finally collecting in a layer over the melted fat.

After all the alcohol has passed in this manner into the flask containing the fat, disconnect the flask from which the alcohol has been distilled and attach the tube to a short piece of rubber tubing attached to a right-angled glass tube as in (2) above, and siphon the alcohol layer back into the alcohol distillation flask. Reconnect as at first and again distill the alcohol as in the first operation. When all alcohol has been distilled, siphon it again into the distillation flask and extract in the same manner for the third time.

Discard the fat and retain the alcohol which now contains practically all of the cholesterol and phytosterol originally present in the fat. Concentrate the alcoholic solution to about 250 cc. and add 20 cc. of KOH solution (1 : 1) to the boiling liquid. Boil for 10 minutes to insure complete saponification of the fat, *cool to room temperature* and pour into a large separatory funnel containing 500 cc. of warm ether. Shake to insure thorough mixing and add 500 cc. of water. Rotate the funnel gently to avoid the formation of persistent emulsions, but mix the water thoroughly with the alcohol-ether-soap solution. A clear, sharp separation takes place at once. Draw off the soap solution and wash the ether layer with 300 cc. of water, avoiding shaking. Repeat the washing of the ether solution with small quantities of water until all soap is removed. Transfer the ether layer to a flask and distill the ether until the volume of liquid remaining in the flask is about 25 cc. Transfer this residue to a tall 50-cc. beaker and continue evaporation until all ether is driven off and the residue is perfectly dry.*

Add 3–5 cc. of acetic anhydride to the residue in the beaker, cover with a watch glass and heat to boiling over a free flame. After boiling for a few seconds, remove the beaker from the flame, cool and add 35 cc. of 60% alcohol by volume. Mix the contents of the beaker thoroughly, filter off the alcoholic solution and wash the precipitate with 60% alcohol. Dissolve the precipitate on the filter with a stream of hot 80% alcohol by volume and wash the insoluble portion well with 80% alcohol. Acetates of cholesterol and phytosterol are dissolved, while the greater portion of the impurities present (including paraffin and paraffin oil, if

* If desired, a tared beaker may be used and the weight of Unsaponifiable Matter determined at this point.

present) remains behind on the filter. Cool the combined filtrate and washings to a temperature of 10–12° C. and let stand at that temperature for 2–3 hours. During this time the acetates of cholesterol and phytosterol crystallize from solution. Collect the crystals on a filter, wash with cold 80% alcohol and then dissolve them in a minimum amount of hot absolute alcohol. Collect the alcoholic solution of the acetates in a small glass evaporating dish, add 2 or 3 drops of water to the solution and heat if not perfectly clear. Let the alcohol evaporate spontaneously, stirring the contents of the dish occasionally to mix with the main body of liquid the deposit of crystals which forms upon the edges. As soon as a good deposit of crystals has formed, collect them upon a hardened filter, wash twice with cold 90% alcohol and dry by suction, drying finally at 100° C. for 30 minutes, and determine the melting point in the apparatus shown in Fig. 17 on page 312, using H_2SO_4 in the outer beaker and glycerol in the inner tube.

The melting point of the first crop of crystals usually gives definite information as to the presence or absence of phytosterol but the conclusion indicated should be confirmed by recrystallizing the crystals from absolute alcohol and again determining their melting point. If the crystals are pure cholesteryl acetate, the melting point of the second crop should agree closely with that of the first. If phytosteryl acetate is present, however, a higher melting point will be noted, as phytosteryl acetate is less soluble in alcohol than cholesteryl acetate. The melting point of cholesteryl acetate is 114° C., that of phytosteryl acetate is 125–137° C.

Soluble Fatty Acids.—This determination is made on the solution after titrating for the saponification number. Place the flask on the water bath and evaporate off the alcohol. Add sufficient 0.5 N HCl so that its volume, plus the net amount used in titrating for the saponification number, will be 1 cc. in excess of the amount required to neutralize the 50 cc. of alcoholic KOH added.* Place on the steam bath until the fatty acids separate into a clear layer. Fill to the neck with hot water and cool in ice water until the cake of fatty acids is thoroughly hardened. Pour the liquid contents of the flask through a filter into a liter flask.

* The amount of 0.5 N HCl to be added = titration of the blank—titration of the sample + 1 cc.

Fill the flask again with hot water, and set on the steam bath until the fatty acids collect on the surface. Cool by immersion in ice water and again filter the liquid into the liter flask. Repeat this treatment with hot water 3 times, cooling and collecting the washings in the liter flask after each treatment. Titrate the combined washings with 0.1 N NaOH and phenolphthalein. Subtract 5 (which corresponds to the excess of 1 cc. of 0.5 N HCl) from the number of cc. of 0.1 N NaOH used. The difference multiplied by 0.00881 gives the weight of soluble acids, as butyric acid. Calculate to percentage.

Insoluble Fatty Acids (Hehner Number.)—Let the flask containing the cake of insoluble fatty acids from the previous determination and the paper through which the soluble fatty acids have been filtered drain and dry for 12 hours. Transfer the cake, with as much of the fatty acids as can be removed from the filter paper, to a weighed, wide-mouthed beaker flask. Then place the funnel containing the filter in the neck of the flask and wash the paper thoroughly with hot absolute alcohol. Remove the funnel, evaporate off the alcohol, dry for 2 hours at 100° C., cool in a desiccator and weigh. Again dry for 2 hours, cool and weigh. If there is any considerable decrease, reheat for 2 hours and weigh again. Calculate the final weight to percentage of insoluble fatty acids.

Soluble Volatile Fatty Acids (Reichert-Meissl Number).—This method is of particular value in the case of substances containing butter fat, which has a very high Reichert-Meissl number. As the determination is entirely empirical, it is necessary to follow the directions exactly.

Reagents.—(1) *NaOH Solution (1:1).*—To 100 grams of NaOH as free as possible from carbonates add 100 cc. of water. Protect the solution from contact with CO_2, let it settle and use only the clear liquid.

(2) *95% Alcohol by Volume.*—Distilled over NaOH.

(3) *Dilute H_2SO_4.*—Dilute 200 cc. of conc. H_2SO_4 to 1 liter with water.

(4) *Barium (or Sodium) Hydroxide Solution.*—Standardize an approximately 0.1 N solution.

(5) *Indicator.*—Dissolve 1 gram of phenolphthalein in 100 cc. of 95% alcohol.

(6) *Pumice Stone.*—Heat small pieces to white heat, plunge in water, and keep under water until used.

Saponification.—Weigh 5.75 cc. (about 5 grams) of the filtered sample into a 300-cc. Erlenmeyer flask;* add 10 cc. of 95% alcohol and 2 cc. of the NaOH solution and heat on the steam bath under a reflux condenser (a glass tube not less than 3 feet long may be used) until saponification is complete, as shown by a clear solution. After saponification, remove the alcohol by evaporation on the steam bath. Avoid possible loss near the end by removing the flask and waving it back and forth in the air. Remove the last traces of alcohol by a stream of air free from CO_2.

Distillation and Titration.—Dissolve the soap obtained above by adding 135 cc. of recently boiled water and warm on the water bath, with occasional shaking, until the solution is clear. Cool to 60–70° C., add 5 cc. of the dil. H_2SO_4, stopper loosely and heat on the water bath until the fatty acids form a clear transparent layer, which may take several hours. Cool to room temperature, add a few pieces of the pumice stone and connect with a glass condenser by means of a bulb tube. Heat slowly with a free flame until ebullition begins and distill, regulating the flame so as to collect 110 cc. of distillate in as nearly 30 minutes as possible. Mix this distillate, filter through a dry filter, and titrate 100 cc. with standard barium or sodium hydroxide solution, using phenolphthalein indicator. The red color should persist for 2–3 minutes.

Multiply the number of cc. of 0.1 N alkali used by 1.1, divide by the weight of fat taken and multiply by 5 to obtain the Reichert-Meissl number. Correct the result by the figure obtained in a blank determination made on all the reagents used.

Insoluble Volatile Fatty Acids (Polenske Number).—For this determination use the method described in Association of Official Agricultural Chemists, "Methods of Analysis" page 291, (1925).

Acetyl Value.—Boil the sample (10–50 grams, depending on its nature) with an equal volume of acetic anhydride in an acetylization flask for 2 hours; pour the mixture into a large beaker con-

* The fat should be warmed if necessary to melt it. Use a warm Mohr pipette for measuring out the liquid fat into the flask, taking care to wipe off the adhering fat and to prevent any fat getting on the sides of the flask. Let come to room temperature and weigh accurately.

taining 500 cc. of water and boil for 30 minutes. To prevent bumping, pass a slow current of CO_2 into the liquid through a finely drawn-out tube reaching nearly to the bottom. Let the mixture separate into 2 layers, siphon off the water, and boil the oily layer with fresh water until it is no longer acid to litmus. Separate the acetylated fat from water, dry at 100–105° C., and filter in the drying oven.

Weigh 2–4 grams of the acetylated fat into a 300-cc. Erlenmeyer flask and saponify with an excess of alcoholic KOH as described under Saponification Number, measuring the alcoholic KOH solution exactly. Evaporate the alcohol after saponification and dissolve the soap in water. Then add to the soap solution a quantity of standard H_2SO_4 exactly corresponding to the amount of alcoholic KOH added; warm gently, filter off the free fatty acids which collect on top, wash with boiling water until the washings are no longer acid and titrate the filtrate with 0.1 N KOH and phenolphthalein. Multiply the number of cc. of alkali by 5.61 and divide by the weight of acetylated oil used, to obtain the acetyl value.

Qualitative Test for Rosin Oil.—Polarize the pure oil, or a definite dilution with petroleum ether, in a 200-mm. tube. Rosin oil has a polarization, in a 200-mm. tube, of from +30° to +40° on the sugar scale (Schmidt and Haensch), while most other oils read between +1° and −1°.

Halphen Test for Cottonseed Oil.—Mix CS_2 containing about 1% of sulfur in solution, with an equal volume of amyl alcohol. Mix equal volumes of this reagent and the oil sample and heat in a bath of boiling, saturated brine for 1–2 hours. This is conveniently accomplished in an acetylization flask. In the presence of as little as 1% of cottonseed oil, a characteristic red or orange-red color is produced.

Lard and lard oil from animals fed on cottonseed meal will give a faint reaction; their fatty acids also give this reaction.

The depth of color is proportional, to a certain extent, to the amount of cottonseed oil present, and by making comparative tests with known mixtures of cottonseed oil some idea as to the amount present can be obtained. Different oils react with different intensities, and oils which have been heated from 200–210° C. react with greatly diminished intensity. Heating for 10

minutes at 250° C. renders cottonseed oil incapable of giving the reaction.

NOTES.—(1) Blown cottonseed oil and old, rancid oil cannot be identified by this test.

(2) Kapok and Baoban oils also give similar color reactions.

(3) A blank test should always be conducted under the same conditions on a pure sample of the oil being tested and also on a pure oil to which has been added a little cottonseed oil.

Tests for Peanut Oil.—RENARD TEST.—Weigh 20 grams of the oil into an Erlenmeyer flask. Saponify with alcoholic KOH solution, neutralize exactly with dilute acetic acid (1:3) and phenolphthalein and wash into an 800–1000-cc. flask containing a boiling mixture of 100 cc. of water and 120 cc. of 20% lead acetate solution. Boil for a minute and then cool the precipitated soap by immersing the flask in water, occasionally giving it a whirling motion to cause the soap to stick to the sides of the flask. After the flask has cooled, decant the water and excess of Pb acetate solution and wash the Pb soap with cold water and then 90% alcohol by volume. Add 20 cc. of ether, cork and let stand for some time until the soap is disintegrated. Heat on the water bath with a reflux condenser, and boil for about 6 minutes. In the case of oils, most of the soap will be dissolved; with lards, which contain much stearin, part of the soap will be left undissolved. Cool the ether solution of soap to 15–17° C. and let stand until all insoluble soaps have separated out (about 12 hours).

Filter on a Büchner funnel and thoroughly wash the insoluble Pb soaps with ether. Wash the ether-insoluble Pb soaps into a separatory funnel by means of a jet of ether, alternating at the end of the operation, if the soaps stick to the paper, with dil. HCl (1:3). Add sufficient HCl (1:3) so that the total volume of the latter amounts to about 200 cc. and enough ether to make its total volume 150–200 cc. and shake vigorously for several minutes. Let the layers separate, run off the acid layer, and wash the ether once with 100 cc. of the dil. HCl and then with several portions of water until the water washings are no longer acid to methyl orange. If a few undecomposed lumps of Pb soap remain (indicated by solid particles remaining after the third washing with water), break these up by running off almost all the water layer

and then add a little conc. HCl; shake and then continue washing with water as before. Distill the ether from the solution of insoluble fatty acids and dry the latter in the flask by adding a little absolute alcohol and evaporating on the steam bath. Dissolve the dry fatty acids by warming with 100 cc. of 90% alcohol by volume and cool slowly to 15° C., shaking to aid crystallization. Let stand at 15° C. for 30 minutes. In the presence of peanut oil, crystals of arachidic acid will separate from the solution.

Filter and wash the precipitate twice with 10 cc. of 90% alcohol by volume, and then with 70% alcohol by volume, taking care to maintain the arachidic acid and the wash solution at a definite temperature in order to apply solubility corrections given below. Dissolve the arachidic acid upon the filter with boiling absolute alcohol, evaporate to dryness in a weighed dish, dry and weigh. Add to the weight 0.0025 gram for each 10 cc. of 90% alcohol used in the crystallization and washing, if conducted at 15° C.; if conducted at 20° C., add 0.0045 gram for each 10 cc. The melting point of arachidic acid thus obtained is 71–72° C. Twenty times the weight of arachidic acid will give the approximate amount of peanut oil present. Arachidic acid has a characteristic appearance and may be identified microscopically. As little as 5–10% of peanut oil can be detected by this method.

It is advisable to run a blank on pure peanut oil along with the test.

Bellier Test.*—Weigh 1 gram of the sample into a long test-tube. Add 5 cc. of alcoholic KOH solution. Boil gently over a small flame holding the tube in the hand until saponification is complete, as shown by homogeneous solution (generally 3–5 minutes). Add the proper amount of acetic acid (see below) to exactly neutralize the 5 cc. of alcoholic KOH. Mix well, cool rapidly in water at about 17° C. and let stand in the water for at least 30 minutes, shaking occasionally. Then add 50 cc. of 70% alcohol containing 1% by volume of conc. HCl and again place in the water for 1 hour. If no peanut oil is present, a clear or opalescent liquid is formed. If more than 10% of peanut oil is present, a flocculent, crystalline precipitate remains. Even with 5% of peanut oil a distinct precipitate remains and separates on standing.

* Allen: "Commercial Organic Analysis," 4th ed., **2**, 99.

Solutions.—(1) *Alcoholic KOH:* Dissolve 8.5 grams of pure KOH in 70% alcohol, and dilute to 100 cc. with the alcohol.

(2) *Acetic Acid:* This should be of such strength that 1.5 cc. will exactly neutralize 5 cc. of the above solution. The dilute acetic acid reagent (4:10) is approximately the correct strength but should be tested against the alcoholic KOH.

Tests for Sesame Oil.—Baudouin Test.—Dissolve 0.1 gram of finely powdered sugar in 10 cc. of conc. HCl in a test-tube. Add 10 cc. of the sample to be tested. Shake thoroughly for 1 minute and let stand for 10 minutes. The aqueous solution separates almost immediately and in the presence of even minute quantities of sesame oil it is colored crimson.

Note.—Some olive oils, especially those from Spain or Africa, give pink or crimson colors. These can be differentiated from the color due to sesame oil by the Villavecchia tests given below.

Villavecchia and Fabris Tests.—The original test as proposed by Baudouin has been modified by Villavecchia and Fabris and is usually carried out according to one of the following modifications:

(1) Place 0.1 cc. of a 2% alcoholic solution of furfural in a test-tube. Add 10 cc. of the oil and 10 cc. of conc. HCl. Shake for 15 seconds and let settle for 10 minutes. In the presence of even 1% of sesame oil the aqueous layer is a distinct crimson color, and in the absence of sesame oil the lower layer is either colorless or at most, in the case of rancid pure olive oils, a dirty yellow color. If a crimson color is obtained, add 10 cc. of water, shake, and again observe the color. If the crimson color disappears, sesame oil is not present.

(2) Mix 0.1 cc. of 2% alcoholic furfural solution with 10 cc. of the oil and add 1 cc. of conc. HCl. Agitate thoroughly and add 10 cc. of $CHCl_3$. The aqueous layer will float on top and in the presence of sesame oil will be colored crimson.

Note.—We have found that this method produces a slight coloration with certain olive oils claimed to be pure. Furthermore, the oils in question gave negative results by the Bellier reaction described below.

Bellier Test.*—To 50 cc. of water, add 100 cc. of conc. H_2SO_4, cool and add 10 cc. of 40% formaldehyde solution. Mix

* *Ann. chim. anal.*, 217 (1899).

equal parts of the oil and the above reagent by stirring. In the presence of sesame oil the emulsion slowly becomes colored a very intense, stable blue-black. With olive oil, peanut oil, cottonseed oil and walnut oil, the emulsion produced is more or less yellow.

It is stated that the percentage of sesame oil can be determined with this reaction when working with a comparatively pure olive oil. With olive oil containing 2% of sesame oil the color of the emulsion is a rather dark gray after 5 or 10 minutes. The acid which separates is a blackish brown. With 5% of sesame oil, the mixture becomes a very dark black gray and the acid which separates is black tinged with blue.

Emery Test for Beef Fat in Lard.—Weigh 5 grams of melted fat into a glass-stoppered, 25-cc. cylinder about 150–175 mm. tall. Add warm ether up to the 25-cc. mark, stopper securely and shake until the fat is completely dissolved. Let the cylinder stand for about 18 hours at a temperature of 16–20° C., during which time some of the solid glycerides will crystallize out. Decant the clear solution carefully from the crystals, wash with three 5-cc. portions of cold ether, avoiding breaking up the deposit during the first two washings. Agitate the crystals with a third portion of ether and transfer to a small filter. Wash on the paper with successive small amounts of cold ether until 15–20 cc. have been used, then remove the last traces of ether by means of slight suction on the stem of the funnel. Break up any large lumps and let the deposit dry.

When thoroughly dry, pulverize the glycerides and take their melting point in a closed 1-mm. tube, using an apparatus similar to that in Fig. 17 (p. 312). Heat the water in the beaker rapidly to about 55° C. and maintain that temperature until the thermometer carrying the melting-point tube registers 50–55° C.; then heat again and carry the temperature of the outer bath somewhat rapidly to 67° C., and remove the lamp. The melting point of the crystals is regarded as that point where the fused substance becomes perfectly clear and transparent. A dark background placed about 4 inches from the apparatus will prove of advantage. When the melting point of the glycerides obtained by this method is below 63.4° C., the presence of beef fat should be suspected, while a melting point of 63° C., or below, can be regarded as positive evidence that the sample is not pure lard. It is advisable to

carry out this method with a control sample of pure lard in connection with each batch of samples analyzed.

Fish and Marine Animal Oils in Vegetable Oils.—This test is only applicable in the absence of metallic salts.

Dissolve in a test-tube about 6 grams of the sample in 12 cc. of a mixture of equal parts of $CHCl_3$ and glacial acetic acid. Add bromine drop by drop, until a slight excess is indicated by the color, keeping the solution at about 20° C. Let stand 15 minutes or more and then place the test-tube in boiling water. If vegetable oils only are present, the solution will become perfectly clear, while fish oils will remain cloudy or contain a precipitate due to the presence of insoluble bromides.

Reference.—Association of Official Agricultural Chemists: "Methods of Analysis" (1925).

LUBRICATING OILS

General.—This method applies to the testing and analysis of lubricating oils, such as engine, machine, turbine, cylinder oils, etc. It does not apply to fuel and burning oils. For the determination of carbon residue in automobile crank case and gas engine oils, see page 339.

All tests should be made in duplicate unless the amount of sample is insufficient.

Gravity.—The gravity of lubricating oils is usually determined as degrees Baumé. The A. P. I. (American Petroleum Institute) hydrometers and gravity tables are based on the modulus 141.5 and have been adopted as standard for all petroleum products. The relation between specific gravity and Baumé gravity is expressed by the formula:

$$\text{Gravity Baumé} = \frac{141.5}{\text{sp.gr.}} - 131.5.$$

Determine the gravity by means of a Baumé hydrometer if possible. If the oil is too light for this, use a Westphal balance. In the case of thick oils, use a hydrometer and let it remain in the oil at least 0.5 hour, so that it will sink as far as possible. Place the hydrometer in the oil carefully and let it sink gradually of its own weight. Never push it down below its final point of equilibrium. Use a cylinder sufficiently large so that the hydrometer does not touch the sides, and also use a sufficient volume of oil so that the hydrometer does not come nearer than within 0.5

inch of the bottom when at rest. Take the reading of the hydrometer at the point where the lower meniscus of the oil touches the scale. If the oil is not too thick, bring it to exactly 60° F. before reading the hydrometer or balance; otherwise determine the temperature of the oil at the time of reading the hydrometer and correct the reading to 60° F. (15.5° C.). Tagliabue's "Manual for Inspectors of Coal Oil" gives readings at 60° F. for any gravity from 20 to 100° Bé. between temperatures of 20 and 109° F.

In using the Westphal balance, be sure that the plummet is completely submerged and does not touch the sides or bottom of the cylinder containing the oil. Have the temperature of the oil at 60° F. From the sp. gr. found by the balance calculate the gr. Bé. from the above formula.

NOTES.—(1) The Westphal should be leveled so that the plummet in air just balances the arm at zero. If the weights are accurate, the reading in distilled water at 60° F. should be 1.0000. In case the reading in water is different from this, correct the observed reading on the sample by dividing it by the reading of the balance in water.

(2) For liquids lighter than water *other than petroleum products* the modulus 140 is standard and the formula is:

$$\text{Gravity Baumé} = \frac{140°}{\text{sp.gr.}} - 130°.$$

Care must be taken not to confuse hydrometers of the two different types nor to use the latter on petroleum oils.

Flash Point.—Determine the flash point in the Cleveland open-cup tester. The apparatus consists of a spun brass or cast-iron cup, $1\frac{3}{8}$ inches high by $2\frac{1}{2}$ inches in diameter, heated from below by a Tirrill burner protected from drafts. Fill the cup with the oil to within about $\frac{3}{8}$ inch of the top. Use an accurate Fahrenheit thermometer scaled for *1-inch* immersion. Immerse the thermometer in the center of the oil at sufficient depth so that the surface of the oil is at the 1-inch mark. (The bulb of the thermometer should be approximately 0.25 inch from the bottom of the cup.) The rate of heating should be between 9 and 11° F. per minute. At intervals of about 5°, when approaching the flash point, sweep a tiny flame about $\frac{5}{32}$ inch in diameter and not more than 0.5 inch long slowly* and steadily across the

* It should require about 1 second for the passage of the flame across the top.

cup at a distance of about $\frac{3}{8}$ inch from the surface of the oil. Do not breathe on the oil. Record as the flash point the first temperature at which a puff of blue flame appears and runs around the cup and then goes out. (The true flash must not be confused with a bluish halo which sometimes surrounds the test flame.)

NOTE.—It is important that the rate of heating should be even, and the test flame should not be placed directly upon the surface of the oil nor held momentarily in any one place over the oil, since this will cause local superheating.

Fire Point.—Continue heating after the flash point has been determined, applying the test flame at intervals of 5°. Take as the fire point the point at which the oil will first take fire and continue to burn for 5 seconds or more. This varies from 15–80° higher than the flash point, depending upon the nature of the oil.*

Cloud Test.—The cloud test indicates the temperature at which solid matter begins to crystallize out. It should be used only for oils which are transparent in layers 1.5 inches deep.

Cut off the neck and shoulder of a 4-oz. oil bottle and fill with the oil to a depth of 1–$1\frac{1}{4}$ inches. The oil must be at least 25° F. above the approximate cloud point. The thermometer used is the so-called "cloud test thermometer," especially made for testing oils, with a bulb $\frac{1}{4}$–$\frac{3}{4}$-inch long. Insert the thermometer through a perforated cork so that it is held centrally in the bottle with the lower end of the bulb 0.5 inch from the bottom. Then place the whole in a metal or glass jacket 4–5 inches high, having an inside diameter 0.5 inch larger than the outside diameter of the oil bottle. Place a disc of felt, cork, or wax 0.25 inch thick in the bottom of the jacket and fit a ring of cork or felt on the inner bottle 1 inch from the bottom. The inner bottle must not touch the sides of the jacket at any point. Then place the whole apparatus in a freezing mixture (see note 2, p. 330) and at every drop in temperature of 2° F. when near the expected cloud test, remove the oil bottle from the jacket, quickly inspect and return it, taking care not to disturb the oil by removing the thermometer or otherwise. The bottle should not be out of the jacket more than 3 seconds.

* With mineral oils the fire point is generally about 10 % higher than the flash point on the Fahrenheit scale.

When the lower half of the sample becomes opaque through chilling, read the thermometer. Report this reading as the cloud test of the sample.

NOTE.—If the oil contains any water, misleading results will be obtained. It should, therefore, immediately before making the test, be heated momentarily to 150° C. and then cooled.

Pour Test.—The pour test indicates the temperature at which the oil will just flow under definite conditions. In making this test use the same apparatus as for the Cloud Test. In practically all cases the cloud test is higher than the pour test.

Bring the oil to a temperature of 90° F. (or to 15° F. above the pour point, if the latter is above 75° F.). Pour the warm oil into the test bottle to a height of 2–2¼ inches. Adjust the thermometer in the stopper of the bottle with the thermometer bulb immersed so that the beginning of the capillary is ⅛ inch below the surface of the oil; then place in the jacket as previously described and put the whole in the freezing mixture, which should be at a temperature not less than 15° or more than 30° F. below the pour point of the oil. Not more than 1 inch of the jacket should project out of the freezing mixture.

After the oil has cooled enough to allow the formation of paraffin wax crystals, take care not to disturb the mass of the oil nor to permit the thermometer to shift in the oil. Any disturbance of the spongy network of wax crystals will cause too low and fictitious results.

At each thermometer reading which is a multiple of 5° F. remove the test bottle from the jacket carefully and tilt it just enough to determine whether the oil around the thermometer flows when the jar is tilted slightly. Replace the bottle in the jacket at once. The complete operation of removal and replacement must not require more than 3 seconds. As soon as the oil around the thermometer does not flow when the jar is tilted slightly, hold the jar in a horizontal position for exactly 5 seconds and observe carefully. If the oil around the thermometer shows any movement under these conditions, replace the test jar immediately in the jacket and repeat the same procedure at the next temperature reading 5° F. lower. In some cases the first movement of the oil is not around the thermometer but from the sides of the test bottle. In such cases this movement shall be

considered in making the test. As soon as a temperature is reached at which the oil around the thermometer shows no movement when the test bottle is held in a horizontal position for exactly 5 seconds, stop the test. Record as the Pour Point the last reading of the thermometer at which the oil around the thermometer shows any movement when the test bottle is held in a horizontal position for exactly 5 seconds. It is to be noted that the pour point is the temperature 5° F. above the solid point, the temperature at which the test is discontinued.

NOTES.—(1) The cold should preferably be applied so that the pour test shall be completed in about 0.5 hour.

(2) Materials used in the freezing mixture may be ice with calcium chloride crystals or salt, or solid CO_2 with acetone.

For oils solidifying above 35° F. use snow or cracked ice and water; from +35° to +15° use finely cracked ice with about 5% its volume of salt; from +15° to −5° use 1 part salt, 3 parts ice. The salt should be very dry and fine enough to pass a 20-mesh sieve. It is possible to reach −25° F. with a mixture of ice and calcium chloride crystals, but for temperatures below −5° it is better to use solid CO_2 and acetone as follows:

Take a sufficient amount of dry acetone and put it into a covered copper or Pyrex glass beaker. Place the beaker in an ice-salt mixture, and when cooled to +10° F. or lower, add solid CO_2, little by little, until the desired temperature is reached. Solid CO_2 is obtained by inverting an ordinary liquefied-CO_2 cylinder, opening the valve carefully and letting the liquid run out into a chamois or canvas bag. Temperatures of −80° F. may be reached by this method.

Cold Test.—Use the oil cylinder as described in the Cloud Test. Add to it 1 ounce of oil (28 cc.). Place the oil in the bottle directly in the freezing mixture (see note 2 above) and freeze solid with a cold-test thermometer immersed in it. When the oil has become solid throughout, let stand 0.5 hour.* Remove the bottle from the freezing mixture. Stir the oil thoroughly, as soon as it has become soft enough to permit, holding the bottle by the neck in the left hand with a piece of waste which prevents the heat of the hand from warming the oil. Continue stirring, tipping the bottle at frequent intervals to an angle of 45 deg. below the horizontal; withdraw the thermometer up

* The oil should be cooled to at least 10° below its cold test. If, therefore, the cold test is first found to be near the temperature to which the oil has been cooled for 0.5 hour, repeat the test, first cooling the oil 10° lower for 0.5 hour.

through the waste just far enough to see the top of the mercury column and note the temperature at which the oil will just run from one end of the bottle to the other. Take this point as the Cold Test.

NOTES.—(1) To get comparative results the above directions should be followed exactly, and even in this case there is a considerable personal factor entering into the determination.

(2) The 4-ounce oil bottles used should be cut off as near the neck as possible, each one having a mark on the side indicating how much oil is to be taken for the cold test. Determine the position of this mark by placing 28 cc. of water in the bottle and making a mark at the upper surface of the water. Be sure the bottle is on a perfectly level place when the mark is made.

Viscosity.—Determine the viscosity with the Saybolt Universal Viscosimeter. The temperature is generally specified for different grades of oils. Unless otherwise requested, the following temperatures are to be employed:

212° F.—Calender, Crane, Crank Case, Cylinder (Steam) and Valve Oils.

130° F.—Black (Dark Lubricating Oil), Air Compressor and Journal Oils.

100° F.—Automobile, Crusher, Cutting, Dynamo, Engine, Froth, Governor, Loom, Machinery, Shafting, Sperm, Spindle, Transformer, Turbine, and Whale Oils.

MANIPULATION.—Have the viscosimeter *level.* Bring the water bath of the viscosimeter to the required temperature. Strain the oil through muslin into a tin cup and heat in the cup to the required temperature, stirring with the thermometer. Clean out the tube of the instrument with some of the strained oil to be tested, using the plunger.

Place the cork in the lower outlet coupling tube just far enough to make it air-tight but not so far as nearly to touch the small outlet jet of the tube proper. Between $\frac{1}{8}$ and $\frac{1}{4}$ inch should be enough. Pour the heated oil from the tin cup through the strainer into the tube of the viscosimeter until it overflows into the oil cup up to and above the upper edge of the tube proper. Again note that the water bath is at the proper temperature. Stir the oil in the upper tube with the thermometer until it is exactly at the correct temperature, then remove the thermometer and draw off from the overflow tube with a pipette all surplus

oil down to and below the upper edge of the inner tube. This always insures the same starting head of oil. Place the 60-cc. flask beneath and directly in line with the outlet jet and as close to the tube as is practical to permit of room for drawing the cork. Hold a stop watch in the left hand, and with a twisting motion remove the cork quickly with the right hand, starting the watch simultaneously. Stir the water in the jacket during the test and move the flask, if necessary, so that the stream of oil strikes the side of the neck and does not cause foaming. Note the exact instant at which the oil rises to the 60-cc. mark in the flask, and stop the watch. The time elapsed for 60 cc. of oil to flow from the viscosimeter is its viscosity at the given temperature. Express results in seconds.

NOTES.—(1) Before each test clean out the tube of the instrument with some of the oil to be tested, always straining the oil first, and before removing the cork note that the oil and bath are at the proper temperature and that the 60-cc. flask is free from oil.

(2) The Universal instrument is not intended to be used on oils at temperatures below 100° F. (see p. 245).

Saponifiable Oil.—Ordinarily this determination is unnecessary except on cylinder oils or other compounded oils. It should *always* be run in duplicate together with duplicate blanks of the alcoholic KOH.

For cylinder oils and other heavy, dark-colored oils weigh out 2 portions of about 20 grams each in a 300-cc. Erlenmeyer flask. Add to each flask 25 cc. (see note 2) of approximately 0.5 N alcoholic KOH, accurately delivered from a pipette. Connect the flask with a clean cork stopper to a Soxhlet extractor and pour into the extractor just enough pure benzene to fill the extractor and cause it to siphon over, and about 5 cc. additional, then connect the Soxhlet extractor to a reflux condenser. The benzene is not absolutely necessary but often makes it easier to determine the end-point in titrating with heavy dark-colored oils. If the benzene is not used, the flask may be connected directly to the reflux condenser (see notes 1 and 2).

Into 2 other similar clean flasks run from the same pipette 25 cc. of alcoholic KOH solution for blanks. If benzene is used in the determination, add the same amount of benzene to the blanks.

After connecting the flasks to reflux condensers, boil gently with a low flame for at least 16 hours, agitating frequently. The agitation is important, especially if benzene is not used, to insure mixing and prevent caking. Then remove the flasks rinsing into them with a few cc. of neutral alcohol any liquid that may have spattered up on the tip of the condenser or extractor. Titrate each while hot with 0.5 N acid and phenolphthalein until the pink color disappears permanently. The absence of the pink color may be determined by letting the solution stand at rest for about 1 minute and noting the color of the lower layer. From the average titration required by the 2 blanks subtract the titrations required by each of the other solutions, respectively. The difference represents the amount of KOH absorbed by the saponifiable oil. Report the Saponification Value (milligrams of KOH per gram of oil) and also the percentage of Saponifiable Oil.

CALCULATIONS.—1 cc. 0.5 N acid = 28.05 mg. KOH.
= 0.144 gram tallow oil.

NOTES.—(1) Ordinary benzene (benzol) may be purified for use as follows: Add a stick of KOH to 1 liter of the benzene and boil under a reflux condenser for 1 hour. Cool and transfer to a large separatory funnel. Add enough water to form 2 layers and draw off the lower layer. Wash the benzene layer once with water, transfer it to a distillation flask and distill up to 82° C., discarding the residue.

(2) The above details are for heavy cylinder oils containing up to 10% of tallow oil. Lighter oils do not need to saponify so long, and the benzene may be omitted. The blanks in this case should also have benzene omitted. For a light cutting oil 1–2 hours is sufficient. For oils containing more than 10% saponifiable, use less than 20 grams for the determination. With a little experience the analyst can judge about how much oil to weigh out and how long to saponify it.

(3) It is customary to calculate the saponifiable oil in cylinder oils to tallow oil (saponification value 195) although sometimes other oils are used. With the exception of wool grease, however, their saponification numbers are approximately the same and the above calculations will show the amount present. In the case of wool grease (average saponification value 102) the following factor should be used:

1 cc. 0.5 N acid = 0.275 gram wool grease.

Wool grease may be recognized by its characteristic odor on heating. If, in compounding the oil, a mixture of wool grease and some other fatty oil is employed, it is impossible by analysis to determine the relative proportions, and the titration should be calculated both as wool grease and as tallow oil. The actual amount present will lie between these figures.

(4) The saponification may be conducted in pressure flasks instead of by the above procedure. In this case weigh the sample into the pressure flask, add the alcoholic KOH (but not benzene), clamp tightly, and place the flask in a steam or hot-water bath. Eight hours are sufficiently long for a cylinder oil. A blank should be run in a separate pressure flask. Cover the flasks with a heavy cloth to prevent accident and do not open them until they are cold.

(5) In the case of oils containing wool grease, the saponification should always be conducted in a pressure flask* to obtain accurate results, as by the ordinary method it is very difficult to saponify the wool grease completely.

Residue Insoluble in Gasoline.—Unless otherwise specified carry out this test on cylinder oils as follows: Shake 5 cc. of the oil with 100 cc. of ordinary gasoline and let stand for 1 hour. There should be no deposit or precipitation of tarry or other foreign matter.

The quantitative estimation is carried out as follows: Weigh out approximately 5 grams of oil into a small beaker. Transfer by means of 86° Bé. naphtha to a 100-cc. graduated cylinder. Fill to the mark with 86° Bé naphtha. Agitate several times until the oil and naphtha are thoroughly mixed. Stopper and let stand for whatever time is specified (generally 1 hour). Filter through a filter paper which has been dried at 100° C. for 2 hours, cooled and weighed in a weighing bottle. Wash the cylinder out with 86° Bé naphtha and pour the washings through the filter paper. Wash the paper thoroughly with the naphtha to remove all traces of oil. Dry in the air and then at 100° C., cool in a desiccator and weigh in the weighing bottle. (If desired it may then be ignited and weighed to determine the amount of mineral matter, dirt, etc.)

NOTE.—86° naphtha is *highly inflammable* and must not be used in the *same room* with any flame.

Mineral Acid.—Weigh 25–50 grams of oil into a 500-cc. separatory funnel, add 300 cc. of hot distilled water, recently boiled, and shake thoroughly. Titrate the water while still hot with 0.1 N NaOH and phenolphthalein. Run a blank on the same amount of hot water and subtract the blank titration from the previous. Calculate the difference to H_2SO_4.

* See page 361.

CALCULATION.—1 cc. 0.1 N NaOH = 0.0049 gram H_2SO_4.

Total Acid.—Weigh approximately 10 grams of the oil into a flask and add 50 cc. of a mixture of equal volumes of water and 95% alcohol which has been neutralized with very dilute NaOH solution. Heat to boiling, agitate the flask thoroughly, and titrate while hot with 0.1 N NaOH. For ordinary oils phenolphthalein may be used as an indicator, but with dark-colored oils the end-point is more easily determined by means of alkali blue 6 B.

Free Fatty Acid.—Calculate the number of cc. of 0.1 N NaOH required for 1 gram of the sample in the Total Acid determination and also in the Mineral Acid determination. Subtract the latter from the former and calculate the difference to oleic acid.

CALCULATION.—1 cc. 0.1 N NaOH = 0.0282 gram Oleic Acid.

Corrosion Test.—Heat to redness in a Tirrill flame a clean strip of pure copper about 0.5 inch wide and 2 inches long and while red hot drop into alcohol. Then let the strip dry as quickly as possible in the air and drop it into a sample of the oil contained in a test-tube. About $\frac{1}{2}$ the length of the Cu strip should be submerged. Close the test-tube with a stopper and let stand for 24 hours. At the end of this time remove the Cu strip and wash clean with neutral gasoline. Then compare it with a similar strip freshly cleaned as previously described. No discoloration of the test strip should be shown by this comparison.

Heat Test.—This test is particularly for transformer oils. Place 100 cc. of the oil in a 300-cc. beaker and heat with a Tirrill burner gradually and uniformly at the rate of 8–10° F. per minute until a temperature of 450° F. is reached. Then let the oil cool and pour the contents of the beaker, after stirring thoroughly, into a 100-cc. cylinder. Let stand for 12 hours at room temperature, then hold toward a strong light and examine for deposit, giving the cylinder a slight rotary motion. If there is a trace of deposit it will be seen to rise from the bottom.

Emulsification Test.—Certain oils, which otherwise have good lubricating properties, exhibit the property of emulsifying with hot water or steam to an extent which may seriously interfere with their suitability for lubrication. It is often important, therefore, to determine the resistance to emulsification. A simple

apparatus* for making the test is shown in Fig. 18. *G* is a liter round-bottomed flask heated from below with a Tirrill burner. *D* is a 1 by 8 inch test-tube graduated in cc. from 20 to 50 cc. The 2 jars *E* and *H* are glass battery jars of 3-liter capacity (or gallon bottles with the top cut off). The end of the glass tube dipping into the test-tube should be cut off at an angle of 30 deg.

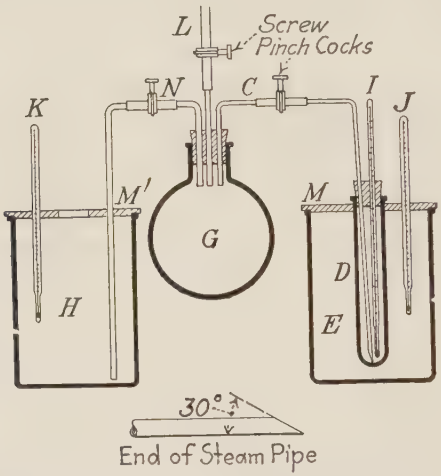


FIG. 18.—Apparatus for Emulsification Test of Oils.

PROCEDURE.—Generate steam in the flask *G*, carefully fill the bath *H* with water, and keep the temperature at 200–203° F. by means of steam. Fill the other bath *E* with approximately 3 liters of water and adjust the temperature to 67° F. Place 20 cc. of the oil to be tested in the graduated test-tube at room temperature and place the tube in the holder *M* of the bath *E*.

Steam out the tube *C* until condensation disappears; then place the cork containing the steam tube and thermometer *I* in the test-tube, with the steam tube touching the bottom of the test-tube and the thermometer 1 inch from the bottom. Admit steam through the steam tube, and control to maintain the emulsion temperature at 190–195° F. This control is effected by manipulating the escape valve *L*. The steam cock in line *C* must be wide open to prevent possible sucking back and the steam

* *Proc. Am. Soc. Testing Materials*, **20**, 1, 418 (1920).

supply must be sufficient to cause a generous discharge at *L*. Continue steaming until the total volume in *D* is between 37–43 cc.* The time required for such steaming must not be less than 4 minutes. If condensed water amounts to 20 cc. in less than 4 minutes, it indicates wet steam or incomplete steaming-out of the line. The usual time required is 4.5–6.5 minutes, depending on the quality of the oil, altitude, etc.

Remove the cork and attachments and transfer the test-tube *D* and contents rapidly to the separating bath (at 200–203° F.). It is extremely important that the bath temperature be kept below 203° F. Take the time on a stop watch at the instant of immersion and observe the progress of separation through the walls of the bath. Examine every 30 seconds until 20 cc. of oil have separated in the top layer. If 20 cc. of oil have not separated in 20 minutes, read the volume of separated oil at that time to the nearest 0.5 cc.

Interpretation of Results.—In interpreting results obtained above, assumption is made that the rate of emulsion separation is directly proportional to the Resistance to Emulsification of the tested oil. In order to establish a basis for comparison, a definite value of 100 is assigned to an oil which, under the conditions of test, separates completely from emulsion in 1 minute. This is equivalent to an emulsion separation rate of 0.33 cc. per second or 20 cc. per minute, and was assigned after experiments demonstrated that the results so obtained were pertinent and relative through a wide range of tests. The value assigned is denoted "Resistance to Emulsification" or "R.E. Value" of the oil.

The Resistance to Emulsification (R.E.) of any oil may be found by substituting in the following formula:

$$\text{R.E.} = \frac{\text{cc. of separated oil} \times 5}{\text{number of minutes}}.$$

Note.—For other emulsification tests see *Bur. Mines Tech. Paper* 323A (1924).

Color (Iodine Method).—The color of petroleum oils may be determined by the following method:

* The apparent volume in the tube near the end of the steaming operation is approximately 12 cc. greater than the actual volume.

Dissolve 10 grams of iodine and 20 grams of KI in water and dilute to 1 liter. Preserve in a glass-stoppered bottle. For very dark oils dilute 1 cc. of the oil with 10 cc. of colorless benzene and then dilute 1 cc. of this solution to 100 cc. with benzene. This is conveniently done in a glass-stoppered, color-comparison tube. In another similar tube place 1 cc. of the standard iodine solution. Dilute with water until the color matches the solution of the oil.

CALCULATION.—

Let A = mg. of iodine per 100 cc. of water in the tube containing the standard solution;

and B = cc. of benzol to 1 cc. of oil;

then, Color $= A(B+1)$.

For lubricating oils and yellow oils a dilution of 1:100 with benzene is sufficient. For nearly colorless oils such as kerosene make the comparison directly without dilution with benzene.

Table XIV shows the National Petroleum Association Standards for lubricating oils and the equivalent iodine colors expressed in milligrams of iodine per 100 cc. of solution.

TABLE XIV—N.P.A. COLOR STANDARDS FOR PETROLEUM OILS

N.P.A. Standard	N.P.A. Color	Iodine Color
A Cylinder, extra light filtered	..	50 (diluted)
D Cylinder, light filtered	..	100 (diluted)
E Cylinder, medium filtered	..	500 (diluted)
G Lily white	1	2.8
H Cream white	1½	5.7
I Extra pale	2	10.8
J Extra lemon pale	..	20.1
K Lemon pale	3	32.1
L Extra orange pale	..	38.4
M Orange pale	4	70.7
N Pale	..	112.0
O Light red	5	195.0
P Dark red	6	300.0
Q Claret red	..	460.0

REFERENCES.—Gill: "Oil Analysis;" Lewkowitsch: "Chemical Technology and Analysis of Oils, Fats and Waxes," **1**; American Society for Testing Materials: Standards; *Bur. Mines, Tech. Paper* 323A (1924).

CARBON RESIDUE IN AUTOMOBILE AND GAS-ENGINE OILS

General.—The amount of "free carbon" or "carbon residue" is an important quality in oils which are to be used for lubrication of gas engines or automobile engines. The method in common use is that of Conradson as described below. The determinations should always be carried out in duplicate.

Apparatus.—The apparatus is shown in Fig. 19 and consists of:

(*a*) A porcelain or glazed silica crucible, wide form, glazed throughout, 25–26-cc. capacity, 46 mm. in diameter.

(*b*) A Skidmore iron crucible, 45-cc. capacity, 65 mm. in diameter, 37–39 mm. high with cover, without delivery tubes, and with one opening closed.

(*c*) A wrought-iron crucible with cover, about 180-cc. capacity, 80 mm. in diameter, 58–60 mm. high. At the bottom of this crucible a layer of sand is placed about 10 mm. deep, or enough to bring the Skidmore crucible with cover on nearly to the top of the wrought-iron crucible.

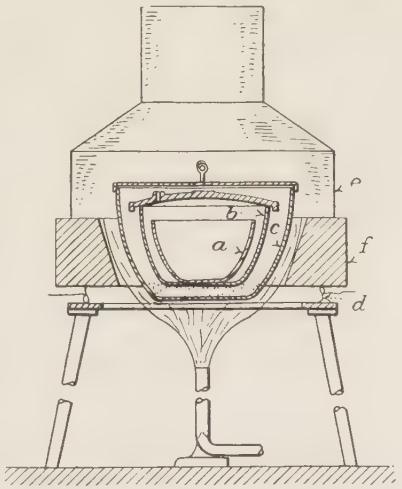


FIG. 19.—Conradson Apparatus for Determining Carbon Residue in Oils.

(*d*) A triangle, pipe-stem covered, with a projection on the side to let the flame reach the crucible on all sides.

(*e*) A sheet-iron or asbestos hood provided with a chimney about 2–$2\frac{1}{2}$ inches high, $2\frac{1}{8}$–$2\frac{1}{4}$ inches in diameter, to distribute the heat uniformly during the process.

(*f*) An asbestos or hollow sheet-iron block, 6–7 inches square, $1\frac{1}{4}$–$1\frac{1}{2}$ inches high, provided with an opening in the center $3\frac{1}{4}$ inches in diameter at the bottom and $3\frac{1}{2}$ inches in diameter at the top.

Determination.—Weigh 10 grams* of the oil in the porcelain or silica crucible, place the latter in the Skidmore crucible and place the 2 crucibles in the larger iron crucible, being careful to have the Skidmore crucible set in the center of the iron crucible with covers over each. Place on the triangle and a suitable stand with the asbestos block, and cover with the sheet-iron or asbestos hood in order to distribute the heat uniformly during the process.

Apply heat from a Tirrill burner or burner with a high flame surrounding the large crucible, as shown in Fig. 19, until the vapors from the oil start to ignite over the crucible. Then slow down the heat so that the vapor (flame) will come off at a uniform rate. The flame from the ignited vapors should not extend over 2 inches above the sheet-iron hood. After the vapor ceases to come off, increase the heat as at the start and continue for 5 minutes, making the lower part of the large crucible red hot, after which let the apparatus cool somewhat before uncovering the crucible. Remove the porcelain crucible, cool in a desiccator and weigh.

The entire process should require about 0.5 hour to complete when the heat is properly regulated. The time will depend somewhat upon the kind of oil tested, as a very thin, rather low flash-point oil will not take as long as a heavy, thick, high flash-point oil.

References.—American Society for Testing Materials: Standards, 620 (1918); *U. S. Bur. Mines, Tech. Paper* 323A.

UNSAPONIFIABLE MATTER IN OILS

General.—The determination of unsaponifiable matter in oils falls into 2 general classes: (1) mineral oil in mixtures of mineral and fatty oils; (2) the natural unsaponifiable matter occurring in animal and vegetable oils. Methods which would give satisfactory results for the first class would hardly be sufficiently accurate to be applied to the determination of the small amount of unsaponifiable matter in the second class. Below are given 3 methods:

* This amount is for oils yielding not over 1.5% of carbon residue. For oils giving 1.5–3.0%, weigh 5 grams; and for those giving over 3.0%, weigh 2 grams.

Method 1 is the ordinary routine method applicable to mixtures of fatty oils with mineral oil.

Method 2 is the method of the Committee on Analysis of Commercial Fats and Oils of the Division of Industrial Chemists and Chemical Engineers of the American Chemical Society, adopted April 14, 1919. It is intended "to aid in determining the commercial valuation of fats and fatty oils in their purchase and sale, based on the fundamental assumption commonly recognized in the trade, namely, that the product is true to name and is not adulterated." It includes "those substances frequently found dissolved in fats and oils which are not saponified by the caustic alkalies and which at the same time are soluble in the ordinary fat solvents. The term includes such substances as the higher alcohols, such as cholesterol which is found in animal fats, phytosterol found in some vegetable fats, paraffin and petroleum oils, etc." This method should be employed in the analysis of commercial oils sold as such.

Method 3 is to be used where a very accurate determination of unsaponifiable matter naturally occurring in animal or vegetable oils is desired.

Method 1.—Weigh out 3–5 grams of the sample into a 300-cc. Erlenmeyer flask, add 50 cc. of 0.5 N alcoholic KOH and saponify under a reflux condenser for several hours. Add a few drops of phenolphthalein to make sure that there is an excess of alcoholic KOH. In case there is not an excess, add 25 cc. more and resaponify. Transfer the contents of the flask to a beaker and evaporate off the alcohol on the steam bath. Dissolve the residual soap in about 50 cc. of hot water and transfer to a separatory funnel, using about 20–30 cc. of water for rinsing the beaker. The total volume should be kept below 100 cc. to minimize the tendency to form emulsions. Cool, add 50 cc. of ether, and shake thoroughly. If the solution does not separate well, add a few cc. of alcohol. Run off the lower soap solution into another separatory funnel. Wash the ether solution with water made slightly alkaline with NaOH. Run the washings into the soap solution in the other separatory funnel and shake this out with a fresh portion of 50 cc. of ether. Repeat the process once again. Combine the 3 ethereal extracts and wash twice with about 15 cc. of water to remove any dissolved soap.

Transfer the washed extracts to a weighed Soxhlet flask, distill off the ether on the water bath and dry the residue at 100° C. to constant weight. As many of the hydrocarbon oils are volatile at 100° C., do not dry any longer than necessary.

NOTES.—(1) If it is suspected that the unsaponifiable matter is contaminated with soap, dissolve it in ether. Transfer to a porcelain or platinum dish, evaporate off the ether and ash the residue. Then titrate the ash with 0.01 N acid and methyl orange and calculate the amount of soap present.

CALCULATION.—1 cc. 0.01 N acid = 0.0032 gram potash soap.

(2) Troublesome emulsions sometimes form during extraction. In such cases it will be found convenient to add a little alcohol or glycerol after shaking, and then impart a slight rotary movement to the separatory funnel without, however, agitating it. In other cases the addition of a little NaOH will break up the emulsion. Sometimes a flocculent layer will appear between the ether solution and the solvent. This, however, does not interfere with the correct determination of the unsaponifiable matter and should be drawn off and considered as soap.

Another method of breaking emulsions is to apply suction. Insert a one-hole stopper with a glass tube in the neck of the funnel and apply suction gently, increasing slowly until the ether boils. Take care not to boil the ether too violently and to avoid sucking back when the suction is released.

(3) Petroleum ether, prepared as described under Method 2 below, may be used in place of ordinary ether. In certain cases, notably with tallow, ordinary ether sometimes fails to extract all the unsaponifiable matter.

Method 2.—Weigh 5 grams (within 0.2 gram) of the sample into a 200-cc. Erlenmeyer flask, add 30 cc. of redistilled ethyl alcohol and 5 cc. of 50% KOH solution and boil the mixture for 1 hour under a reflux condenser. Transfer to a special extraction cylinder (see below) and wash to the 40-cc. mark with redistilled 95% alcohol. Complete the transfer, first with warm, then with cold water, till the total volume is 80 cc. Cool the cylinder and contents to room temperature and add 50 cc. of petroleum ether (see below). Shake *vigorously* for 1 minute and let settle until both layers are clear. The volume of the upper layer should be about 40 cc. Draw off the petroleum ether layer as closely as possible with a slender glass siphon into a 500-cc. separatory funnel. Repeat the extraction at least 4 times more, using 50 cc. of petroleum ether each time. (More extractions than 5 are necessary where the unsaponifiable matter runs high, over 5%, and also in some cases where it is lower than 5% but is extracted with difficulty.)

Wash the combined extracts in a separatory funnel 3 times with 25-cc. portions of 10% alcohol, shaking vigorously each time. Transfer the petroleum ether extract to a wide-mouthed, tared flask and evaporate on the steam bath in a current of air. Dry to constant weight, preferably in a vacuum oven (see p. 314). For ordinary purposes the residue may be dried in a well-ventilated air oven at approximately 105° C.

Test the final residue for solubility in 50 cc. of petroleum ether at room temperature. If there is any insoluble residue, filter and wash with petroleum ether and again evaporate and dry the residue.

NOTES.—(1) *Extraction Cylinder.*—Use a glass-stoppered cylinder about $1\frac{3}{8}$ inches in diameter and 12 inches high and graduated at 40 cc., 80 cc. and 130 cc.

(2) *Petroleum Ether.*—Use redistilled petroleum ether, boiling under 75° C. A blank must be made by evaporating 250 cc. with about 0.25 gram of stearin or other hard fat (previously brought to constant weight by heating and drying as in the actual determination. The blank must not exceed a few milligrams.

(3) In order to secure accurate results the extraction must be accompanied by thorough and vigorous shaking and the 2 phases brought into the most intimate contact possible, otherwise low and disagreeing results may be obtained.

Method 3 (Boemer).—To 100 grams of the oil in a 1000–1500-cc. Erlenmeyer flask add 60 cc. of an aqueous solution of KOH (200 grams dissolved in water and diluted to 300 cc.) and 140 cc. of 95% alcohol. Connect with a reflux condenser and heat on the water bath, shaking at first until the liquid becomes clear. Then heat for 1 hour with occasional shaking. Transfer while yet warm to a 2000-cc. separatory funnel, to which some water has been added, and wash out the Erlenmeyer flask with water, using in all 600 cc. Cool, add 800 cc. of ether, and shake vigorously for 1 minute. In a few minutes the ether solution separates perfectly clear. Draw off the soap and filter the ether (to remove the last traces of soap) into a large Erlenmeyer flask. Distill off the ether, adding, if necessary, one or two pieces of pumice stone. Shake the soap solution three times with 400 cc. of ether, which add to the first ether extract. To the residue left after distilling the ether add 3 cc. of the above KOH solution, and 7 cc. of 95% alcohol, and heat under a reflux condenser for 10 minutes on the

water bath. Transfer to a small separatory funnel, using 20–30 cc. of water and, after cooling, shake out with 2 portions of 100 cc. of ether. Wash the ether three times with 10 cc. of water. After drawing off the last of the water, filter the ethereal solution so as to remove the last drops of water, distill off the ether, and dry the residue in a water oven to constant weight at 100° C.

References.—Lewkowitsch: "Chemical Technology and Analysis of Oils, Fats and Waxes," **1**, 364–367; Boemer-Ubbelohde: "Handbuch der Öle u. Fette," 261–262; Association of Official Agricultural Chemists, "Methods of Analysis," 295 (1925).

CASTOR OIL

General.—Pure castor oil is nearly colorless or pale greenish, very viscous and of high sp. gr. It has also a very high acetyl value, and is strongly dextrorotary. Its saponification value is comparatively low. It is miscible in all proportions with glacial acetic acid and with absolute alcohol. The "constants" of a pure oil should come within the following limits:

Sp. gr. at 15.5° C	0.958–0.970
Saponification number	176–187
Iodine number	81–91
Acetyl value	about 150
Free fatty acid	about 1%

Analysis.—The procedures for the determination of each of the above constants are given on pages 298–320.

Solubility Tests.—(*a*) In glacial acetic acid.

(*b*) In absolute alcohol.

Mix in 2 test-tubes equal parts of the sample with each of the above reagents, respectively. In each case the oil should dissolve completely and show no turbidity.

Note.—Castor oil is generally not adulterated. Adulteration with blown oils (linseed, rape, cottonseed, etc.) would be detected by turbidity in the solubility tests. In the case of suspected addition of rosin oil, determine the unsaponifiable matter, which in pure castor oil is less than 1%. All adulterations would lower the acetyl value.

COD LIVER OIL

General.—Genuine cod liver oil is obtained from the liver of the codfish. The commercial oil often has a dark color and

disagreeable odor and taste. The best medicinal oil is termed "steam liver oil" and is made by heating absolutely fresh livers in jacketed vessels heated by hot water or steam. Crude medicinal oil is filtered and bleached by treatment with Fuller's earth and by exposure to the action of sunlight. Cod liver oil must not be confused with cod oil which may or may not be made from the cod livers.

The color of pure medicinal cod liver oil is pale yellow or light yellow and the best qualities have only a slightly fishy, but not rancid, odor and a not unpleasant taste. The "constants" of pure cod liver oil are as follows:

Sp. gr. at 15.5° C	0.923–0.930
Solidifying point	0–10° C.
Saponification value	168–193
Iodine value	135–181
Refractive index at 15.5° C	1.4800–1.4852
Maumené test	113–116° C.

The *U. S. Pharmacopoeia,* Ninth Edition, requires the following constants for medicinal oil:

Sp. gr. at 25° C	0.918–0.922*
Saponification value	180–190
Iodine value	140–180

A good medicinal oil should have a Reichert-Meissl number less than 0.5; and a higher number, especially one exceeding 1.0, would indicate that the livers employed for the extraction of the oil were not perfectly fresh. Such an oil would have an unpleasant taste.

It is also generally considered that, other things being equal, the higher the iodine value the better the oil. The average iodine value of a good medicinal, non-congealing oil is about 167. The amount of unsaponifiable matter should not, as a rule, exceed 1.5%. Larger amounts, in the absence of mineral oil, indicate admixture with other liver oils, such as shark liver oil.

Solubility.—Cod liver oil is slightly soluble in alcohol and soluble in ether, CCl_4, CS_2 and ethyl acetate.

Specific Gravity.—See page 298.

Saponification Value.—See page 309.

* Equivalent to 0.924–0.928 at 15.5° C.

Iodine Value.—See page 310.

Refractive Index.—See page 299.

Maumené Test.—Follow the procedure on page 351. Since, however, cod liver oil has a very high Maumené test, it should be diluted with an equal volume of pure olive oil and the test run on 50 grams of the mixture. Determine separately the Maumené value of the olive oil and calculate the Maumené value of the cod liver oil as follows:

Let X = Maumené of cod liver oil;
A = Maumené of mixture;
and B = Maumené of olive oil.
Then $X = 2(A - 0.5B)$.

Free Fatty Acids.—See page 311.

Color Tests.—(1) A solution of 1 drop of the oil in 1 cc. of $CHCl_3$ when shaken with 1 drop of conc. H_2SO_4 should acquire a violet-red tint, gradually changing to reddish-brown.

(2) Let 2 or 3 drops of fuming HNO_3 (sp. gr. about 1.44) flow alongside 10–15 drops of the oil on a watch glass. A reddish or purplish color should be produced at the zone of contact. On stirring the mixture with a glass rod, this color should become bright rose-red. This test distinguishes cod liver oil from seal oil, which shows no change in color, and from other fish oils, which become blue.

References.—Lewkowitsch: "Chemical Technology and Analysis of Fats, Oils and Waxes," **2**, 348–370; *U. S. Pharmacopoeia*, 9th ed., 297.

SULFONATED OILS

(Turkey Red Oils)

General.—Sulfonated or sulfated oils are made by treating various oils with H_2SO_4. The excess of acid is then neutralized with alkali and a certain amount of water added. Formerly castor oil was supposed to give a better sulfonated oil than any other but this is now open to dispute, as many other oils have been sulfonated and the resulting product is satisfactory for many purposes. Among them may be mentioned olive oil, maize oil, cottonseed oil, red oil, lard oil, and rosin oil. Sulfonated rosin oil especially has found considerable use in cutting oils. It is to

be noted that the amount of oil in commercial sulfonated oils is generally considerably overstated. A so-called "50% oil" will not generally contain more than 40% of oil, and a 70% oil from 60–65% of oil, etc.

Moisture.—Weigh out 30–40 grams and determine the moisture by the Xylol Method as described on page 358.

Ash.—Weigh a convenient quantity (5–10 grams) into a dish or crucible, ignite gently, allowing the oil to burn, and finally heat at a dull red until all the carbon is consumed. Cool in a desiccator and weigh.

Unsaponifiable Matter (Mineral Oil, etc.).—Weigh approximately 10 grams into a 300-cc. Erlenmeyer flask. Add 5 cc. of approximately normal alcoholic KOH solution. Boil for 1 hour with a reflux condenser. Add 40 cc. of water and cool, transfer to a separatory funnel and shake out at least three times with petroleum ether (naphtha), using 50 cc. each time. Wash the ether layer at least three times, first with slightly alkaline 50% alcohol and then twice with water. If emulsions are formed, add a little alcohol to break them. Finally evaporate the petroleum ether extract in a tared vessel, dry, cool, and weigh.

NOTE.—The petroleum ether should have a boiling point of 40–75° C. and should leave no residue when evaporated on the steam bath. During the saponification, if the contents of the flask bump violently, turn out the flame and let the solution cool, and then add 25 cc. of the petroleum ether and continue the boiling.

Total Alkali.—Weigh 10 grams into a 250-cc. Erlenmeyer flask, dissolve in 150 cc. of water (warm if necessary), add 30 grams of granulated NaCl, 25 cc. of ether, and 5 cc. of methyl orange indicator and titrate with 0.5 N acid. Calculate to mg. of KOH per gram of sample. Call this *A*.

CALCULATION.—1 cc. 0.5 N acid = 28.05 mg. KOH.

Free Sulfur Trioxide.—Weigh out approximately 4 grams in a separatory funnel, add sufficient petroleum ether to dissolve it and shake out several times with 25-cc. portions of a conc. NaCl solution, free from sulfates. Combine the washings, dilute, filter, and determine the SO_3 in the filtrate (salt solution) in the usual way with $BaCl_2$, finally weighing as $BaSO_4$. Calculate to SO_3.

CALCULATION.—$BaSO_4 \times 0.3430 = SO_3$.

Combined Sulfur Trioxide.*—Weigh 8 grams into a 300-cc. Erlenmeyer flask and boil 1 hour under a reflux condenser with 25 cc. of 1 N H_2SO_4. Use glass beads to prevent bumping and shake frequently. Wash the condenser into the flask. To the cooled mixture add about 20 cc. of ether, 100 cc. of water, 30 grams of granulated NaCl, and 5 cc. of methyl orange indicator. Titrate with 0.5 N NaOH. Stopper the flask and shake frequently during the titration. Deduct the amount of H_2SO_4 added from the equivalent of the amount of NaOH required to neutralize and calculate the difference to mg. of KOH per gram of sample. Call this F.

Percentage of combined $SO_3 = 0.1426(F+A)$.

Ammonia.—Weigh 8 grams into a 500-cc. beaker, add 50 cc. of 95% alcohol and several drops of phenolphthalein indicator. Titrate to neutrality with 0.5 N NaOH; boil gently till no more NH_3 is given off (as shown by moist litmus paper), cool, add 0.5 N NaOH again till the pink color persists; again boil to drive off any remaining NH_3 and titrate to the end-point after cooling. Record the total number of cc. of 0.5 N NaOH required. Add 150 cc. of water and 5 cc. of methyl orange indicator and titrate to the acid end-point with 0.5 N acid. The number of cc. of 0.5 N acid required for this titration corresponds to the combined and free fatty acids. Calculate to mg. of KOH per gram of sample. Call this B.

The number of cc. of 0.5 N acid minus the total number of cc. of 0.5 N NaOH used to make alkaline corresponds to the alkali minus the NH_3. (In the case of the presence of NH_4 salts this may be a negative quantity.) Preserve the sign and calculate to mg. of KOH per gram of sample. Call this C.

Percentage of $NH_3 = 0.03036(A-C)$.

Free and Combined Fatty Acids.—B = free and combined fatty acids, expressed in mg. of KOH per gram.

Percentage of free and combined fatty acids† $= 0.5031B$.

$B-A$ = free fatty acids, in mg. of KOH per gram.

Percentage of free fatty acids† $= 0.5031(B-A)$.

* This refers to SO_3 combined with the oil and not to SO_3 present as neutral Na_2SO_4 or $(NH_4)_2SO_4$.

† Calculated as oleic acid.

NOTE.—Other computations may be obtained from the above data as follows:

(1) Percentage of Na_2SO_4 in ash due to combined $SO_3 = 0.1238$ $(C+F+A)$. When C is greater than $(F+A)$, substitute $(F+A)$ for C.

(2) Percentage of Na_2CO_3 in ash due to fixed alkali combined as soap = $0.0946\ [C-(F+A)]$. When the latter term is negative, there can be no carbonate in the ash.

(3) Percentage of Na combined as Soap = $0.041C$.

(4) Percentage of salts and mineral impurities = Ash $-Na_2SO_4-Na_2CO_3$.

(5) Percentage neutralized combined SO_3 = combined $SO_3 \times 1.49$.

Total Fatty Matter.—Calculate the total fatty matter by subtracting from 100% the sum of the percentages of Moisture, Unsaponifiable, NH_3, Sodium as Soap, Neutralized Combined SO_3, and Salts and Mineral Impurities.

NOTE.—If an actual determination of the approximate amount of total fatty oil is desired, save the soap solution left after extracting with petroleum ether in the determination of unsaponifiable matter. Add an excess of HCl to it and shake out with ether 3 times. Wash the ether extracts with water, evaporate the ether in a tared flask, dry and weigh as fatty acids.

Neutral Fat.—Subtract the percentage of Free and Combined Fatty Acids, calculated as oleic acid, from the Total Fatty Matter and report the difference as Neutral Fat.

NOTES.—(1) Report results only to 1 decimal place.

(2) The above (except Free Sulfur Trioxide) are the official methods of the American Leather Chemists' Association.

LARD OIL

General.—Lard oils are generally graded as follows:

1. *Prime Lard Oil.*—Is prepared from prime steam lard and is light straw colored. Also known as Extra Winter Strained. Acidity is low; railroad specifications usually allow 2% oleic acid.

2. *Pure Lard Oil.*—Also a light-colored oil, made from No. 1. lard and white grease.

3. *Extra No. 1 Lard Oil.*—Somewhat darker oil than the above; made from light yellow grease. Specifications generally require not over 10% oleic acid.

4. *No. 1 Lard Oil.*—Deep yellow; made from yellow grease. This grade varies considerably; the oleic acid may run 15% or less, or may go as high as 20%.

5. *No. 2 Lard Oil.*—Brown colored, prepared from brown and gut greases.

6. *Crackling Lard Oil.*—Cheapest grade and made from crackling grease.

For the "constants" of pure lard oil, see page 302.

Specific Gravity.—See page 298.

Saponification Number.—See page 309.

Iodine Number.—See page 310.

Free Fatty Acid.—See page 311.

Cold Test.—When it is desired to determine the cold test use the procedure described on page 330. Some specifications call for a cold test below 45° F. between October 1 and May 1.

OLIVE OIL

General.—Olive oil is obtained from the fruit of the olive tree and its quality depends upon the care with which it is prepared. The best grade of edible oil is known as Virgin Oil. Lower grade oils are frequently known as Salad Oil or Ordinary Table Oil. A still lower grade is used for soap-making. The color varies considerably, commercial oils being of shades from colorless to yellow and the lower grades generally quite green due to dissolved chlorophyll. The "constants" vary somewhat with the grade of oil but generally are within the following limits:

Sp. gr. at 15.5° C	0.914–0.920
Saponification number	185–200
Iodine number	77–93
Acetyl value	5–30
Unsaponifiable matter	0.5–1.5%

The iodine number of high-grade oils should be generally between 81 and 85 and the free fatty acid less than 1%.

Several tests have been recommended for detection of mixtures of other oils with olive oil. Some of these tests depend upon the production of a characteristic color. Such tests, however, should be used with caution and always should be accompanied by a blank test on olive oil of known purity and also on pure olive oil containing varying amounts of the suspected foreign oil.

On account of the high duty on imported edible oil, it is customary to "denature" commercial olive oil which is to be

used for manufacturing purposes. The denaturing is accomplished generally by the addition of a small amount of oil of rosemary which gives it a characteristic odor and unpalatable taste. The amount added is usually too small to have any appreciable effect on the constants of the olive oil. It may be removed if desired by steam distillation or by heating and stirring the oil.

Specific Gravity, Saponification Number, Iodine Number, and Free Fatty Acid.—See pages 298–311.

Elaidin Test.—Place in a test-tube 10 grams of the oil, 5 grams of conc. HNO_3 and 1 gram of mercury, and dissolve the latter by shaking continuously for 3 minutes. Let the mixture stand for 20 minutes and again shake for 1 minute. The behavior of different oils after that time is recorded in the following table:

TABLE XV—ELAIDIN TEST OF OILS

Kind of Oil	Consistence
Olive	Solidified after 60 minutes
Arachis (Peanut)	Solidified after 80 minutes
Sheep's foot	Solidified after 120 minutes
Sesame	Solidified after 185 minutes
Colza (Rape)	Solidified after 185 minutes
Linseed	Forms red, dough-like scum
Cod liver	Becomes doughy, red and forms scum
Whale	Remains unchanged
Hemp seed	Remains unchanged

NOTES.—(1) The test must be made at a temperature not lower than 25° C. and the temperature must be uniform throughout the experiment.

(2) The length of time required for solidification is of far greater importance than the ultimate consistency of elaidin formed.

(3) The test cannot be made quantitative. The age of the oil and the length of time it has been exposed to air and light have an important bearing on the results. It is necessary to carry out the test side by side with an oil of known purity under exactly similar conditions.

Maumené Test.—Weigh accurately 50 grams of the oil into a 250-cc. beaker. Have ready a bottle of conc. H_2SO_4, the exact strength of which has been determined by titration.* Place the bottle of acid and the beaker of oil in a large vessel of water until both have acquired the same temperature, which should be about

* The strength of the acid should be as near 94% as possible.

20° C. Remove the beaker of oil, wipe the outside and place in a "nest" of cardboard having hollow sides stuffed with cotton wool, or in a large beaker lined with cotton wadding. Immerse the bulb of a centigrade thermometer in the oil and note the temperature. Then pipette 10 cc. of conc. H_2SO_4 and let it run rapidly into the oil. The time allowed for emptying of the pipette should be only 1 minute. During this time, stir the oil with the thermometer and continue stirring until no further rise of temperature is observed. Record the highest point, which is easily noticed, as the temperature remains constant for some little time before it begins to fall.

The influence of the concentration of the acid on the result is shown in the following table:

TABLE XVI—EFFECT OF STRENGTH OF ACID ON MAUMENÉ TEST

Kind of Oil	Rise of Temperature Observed with Acid Containing Per Cent of H_2SO_4						
	97.38%	96.71%	95.72%	94.72%	93.75%	92.73%	91.85%
	° C.	° C.	° C.	° C.	° C.	° C.	° C.
Olive, genuine..	42.25	42	39	36.5	34.50	31	28.00
	43.25	.....	.....	.....	.....	.....	29.25
Rape, genuine..	62	61	58	54	50.25	47	40.5
	63	.....	.....	.....	.....	.....	43.0
Olive, impure..	48.5	47.0	43.75	40.25	38.5	35.5	32.5
	.....	47.5	44.25	40.75	39.0	.....	.....

Color Tests.—*Halphen Test* for Cottonseed Oil, see page 321.
Baudoin Test for Sesame Oil, see page 324.
Villavecchia Test for Sesame Oil, see page 324.
Bellier Test for Sesame Oil, see page 324.

Probable Adulterants.—*Cottonseed Oil.*—Shown by high iodine value (100–117), high Maumené figure (variously given from 61 to 84), and positive Halphen Test.

Peanut Oil.—Shown by high iodine value (96–109) and isolation of arachidic acid by Renard Test (see page 322).

Rape Oil.—Shown by high iodine value (94–105) and low saponification value (167–179).

Sesame Oil.—Shown by Baudoin Test.

Poppy-seed Oil.—Shown by high iodine value (134–142) and high Maumené figure (74–78).

NOTE.—Olive oil is characterized by low Maumené and iodine numbers and by solid elaidin.

REFERENCES.—Gill: "Oil Analysis," 5th ed.; Lewkowitsch: "Chemical Technology and Analysis of Oils, Fats and Waxes;" Allen: "Commercial Organic Analysis."

OLEIC ACID

(RED OIL)

Oleic Acid, Olein, Elain or Red Oil is the name applied to the liquid fatty acids separated by processes similar to those used in candle making. Saponification oleic acid is obtained by refrigeration and pressing; distilled oleic acid by the distillation process which, when conducted in contact with the air, partially decomposes it into hydrocarbons. It is largely used in soap-making and for wool oils. It has also recently found considerable use for sulfonating.

The "constants" are as follows:

	Pure	Commercial
Sp. gr. at 15.5° C.	0.898	0.890–0.910
Melting point	14° C.	.....
Molecular weight	282.3	.....
Iodine number	90	80–96
Refractive index at 25° C.	1.4603	.....
Free fatty acids	100%	85–98%
Saponification value	198.7	175–205

Commercial oleic acid varies considerably according to the method of preparing it, but as a general rule the constants should come within the above limits. For determination of the sp. gr., iodine number, saponification value and free fatty acids, see pages 298–311.

STEARIC ACID

General.—Stearic acid or Stearin is the name applied to the mixture of solid fatty acids obtained by processes similar to those

used in candle making. It is a mixture of stearic acid ($C_{17}H_{35}COOH$) and palmitic acid ($C_{15}H_{31}COOH$) and sometimes also contains oleic acid ($C_{17}H_{33}COOH$). As the molecular weight of palmitic is considerably less than that of stearic acid, samples of commercial stearic acid will often show on analysis more than 100% of stearic acid.

The "constants" of pure stearic acid are as follows:

Sp. gr. at $\frac{80° \text{ C.}}{4° \text{ C.}}$	0.8886
Melting point	69.3° C.
Molecular weight	284.3
Iodine number	0
Refractive index at 80° C	1.4300
Saponification number	197.3

Specific Gravity.—It is not generally necessary to determine the sp. gr., but if desired, this may be done by the usual methods. It may be noted that at 11° C. the sp. gr. of stearic acid is the same as water.

Solubility Tests.—Stearic acid should be completely soluble in twenty-five times its weight (or more) of alcohol and in a 5% solution of Na_2CO_3. It is only slightly soluble in petroleum naphtha.

Iodine Number.—Determine the iodine number as on page 310. Although pure stearic acid has no iodine number, the commercial article often shows an appreciable absorption, generally due to the presence of more or less oleic acid and, in the absence of other impurities, the percentage of oleic acid can be calculated directly from the iodine number. As the iodine number of pure oleic acid is 90, the iodine number of a mixture of oleic and stearic acids multiplied by 1.11 will give directly the percentage of oleic acid.

Free Fatty Acids.—Determine the free fatty acids as on page 311 and calculate as stearic acid.

CALCULATION.—1 cc. 0.1 N NaOH = 0.02843 gram stearic acid.

The percentage of free fatty acids calculated as above generally varies between 95 and 100% in commercial stearic acid.

Soap and Mineral Impurities.—Ignite 5 grams of the material in a platinum crucible. Weigh the ash, dissolve it in water and,

if alkaline to methyl orange, titrate with 0.1 N HCl. Calculate to sodium stearate.

CALCULATION.—1 cc. 0.1 N HCl = 0.0306 gram sodium stearate.

Saponification Number.—It is not generally necessary to determine the saponification number. If desired, follow the procedure on page 309. Mineral oils and unsaponifiable matter would be indicated by incomplete solubility in alcohol or Na_2CO_3 solution as well as by a low fatty acid content.

TALLOW

General.—Tallow is the fat of beef or sheep. There is, however, very little pure beef or mutton tallow on the market; most tallow is a mixture of the two. We have prepared in this laboratory samples of pure mutton tallow and pure beef tallow which, on analysis, showed the following results:

	Mutton	Beef
Melting point (open tube)	50° C.	39° C.
Iodine number (Wijs)	32	51
Saponification number	198	198
Free fatty acid (as oleic)	0.48%	1.16%
Ash	None	None
Moisture	None	None

Color.—When it is desired to determine the color, melt some of the sample in a flat Petri dish and let cool quietly so that it will form a cake with a smooth flat surface. Measure the color with the Ives colorimeter or tintometer, specifying in the report which instrument was used.

Melting Point.—Determine the melting point by the open-tube method. Take a small glass tube about 20 mm. long and 1.5 mm. inside diameter, open at both ends. Partly fill the tube by pushing one end of it into the tallow. Wipe any tallow off the outside and have the contents flush with the bottom of the tube. Fasten the tube to the mercury bulb of a thermometer by means of rubber elastics and suspend the thermometer in a beaker of water. The bottom of the thermometer should be 0.5 inch above the bottom of the beaker and there should be sufficient water to

completely cover the tube. Heat the water slowly and note when the tallow just begins to melt and draw up from the bottom of the tube. Report this temperature as the Melting Point.

Iodine Number.—Weigh out 0.4–0.5 gram into a wide-mouthed, glass-stoppered bottle, and determine the iodine number by the Wijs method, as described on page 310.

NOTE.—It is convenient to weigh the tallow on a small watch crystal which can then be placed directly in the bottle.

Saponification Number.—Pour about 2 grams of the melted fat into a weighed Erlenmeyer flask of about 300-cc. capacity. Then take the exact weight of the flask and tallow. Determine the saponification number as on page 309.

Free Fatty Acid.—Weigh 10 grams into an Erlenmeyer flask as above. Add 60 cc. of ethyl alcohol, previously neutralized with 0.1 N NaOH and phenolphthalein. Warm for 0.5 hour on the steam bath with occasional shaking. Titrate with 0.1 N NaOH and phenolphthalein with vigorous shaking until the pink color persists for 1 minute. Calculate the percentage of oleic acid.

CALCULATION.—1 cc. 0.1 N NaOH = 0.0282 gram oleic acid.

Moisture.—Melt some of the tallow in a clean, dry test-tube and heat until it begins to smoke. If any appreciable amount of moisture is present, the melted fat will be turbid and will crackle. In such case, determine the moisture by the Xylol Method (see p. 358).

Ash.—Ignite 2–5 grams gently in a weighed platinum dish, cool in a desiccator and weigh the ash. For accurate results do not let the fat take fire and burn.

Soap.—Dissolve the ash obtained above in water and titrate with 0.1 N HCl and methyl orange. Calculate the titration (if any) to sodium stearate.

CALCULATION.—1 cc. 0.1 N acid = 0.0306 gram Na stearate (soap).

GREASES

Types.—Commercial greases may be divided into the following classes:

A. TALLOW TYPE.—These greases are made up of tallow and more or less of an alkali soap, commonly the Na or K soaps of

palm oil, mixed with a smaller amount of mineral oil. These were the principal types of lubricating grease some years ago, but to-day are less used than the greases of type *B*.

B. Soap-thickened Mineral-Oil Type.—These are the most common journal greases to-day, and are composed of mineral oil of various grades made solid by the addition of Ca or Na soaps. The former soap is more commonly used.

C. Pigmented Greases.—Types *A* or *B* with the addition of a mineral lubricant, usually graphite, mica or talc (asbestine).

D. Rosin-oil Type.—These consist of rosin oil thickened by CaO, or less commonly, by PbO, to which is added more or less mineral oil, either paraffin or asphalt oils being used. These are sticky, usually contain 20-30% of water, and find their chief application as gear greases, where true lubrication is not so essential as prevention of wearing and rattling of the gears. Some very heavy bearings are occasionally lubricated with this type of grease. Tar, pitch, graphite and such fillers as wood pulp and ground cork are often put into these gear greases.

E. Non-fluid Oils.—These are thin greases stiffened to some extent with aluminum oleate or a mixture of soaps, as for instance Na and Ca soaps.

F. Special Greases, such as a mixture of wood pulp and graphite; thin greases of any of the above types mixed with wool or cotton fibers; freak greases containing rubber, etc.

Of the above types *A*, *B*, *C* and *E* are the most important as lubricants.

General.—Note first the odor and the color. The grease should melt to a clear homogeneous fluid and the oil should not melt away from the soap.

Melting Point.—Use an open tube with an interior diameter of 4 mm. and about 80 mm. long. Plunge this into the sample so that a plug of grease about 1 cm. long is left in the glass tube. Then attach the latter by a rubber band to an accurate thermometer, with the grease opposite the mercury bulb. Immerse the thermometer with the tube attached in a beaker of water so that the bottom of the grease is about 5 cm. below the surface. Heat the water slowly at the rate of about 3–4° C. per minute. When the melting point is reached, the plug, which is under a pressure of 5 cm. of water, will slide up in the tube.

NOTE.—If the grease cannot be melted in hot water, use a heating liquid with a higher boiling point. For this purpose glycerine may be added to the water, or a neutral salt such as sodium sulfate dissolved in it.

Moisture (Xylol Method).—Weigh out 10 grams of the grease on a balanced filter paper and place the grease and paper in a 300-cc. Erlenmeyer flask. Add to this 75 cc. of xylol which has previously been saturated with water, as follows:

A convenient quantity of commercial xylol, say 500 cc., is shaken up in a separatory funnel with water and the xylol drawn off and distilled slowly from a distillation flask. From this distillate a small amount of water will separate. The xylol standing above the water is poured off into a glass-stoppered bottle, with a tightly fitting stopper, and preserved for use in moisture determinations.

Connect the flask containing the grease and xylol with a condenser, which must be perfectly dry. Heat the flask gradually in a bath of cylinder oil and distill the xylol and water slowly until the xylol comes over clear, collecting the distillate in a funnel tube with a stem graduated to 0.1 cc. The bulk of the water comes over with the first 10 cc. of distillate. After the distillation is completed, wash down the condenser with water-saturated xylol and tap the funnel tube gently until any small drops of water clinging to the sides are brought down to the bottom. Read the volume of water. Using a 10-gram sample, each 0.1 cc. is equivalent to 1% of water in the grease.

NOTE.—If the mixture gives trouble from frothing, on account of the soap present, add sufficient dry fused and powdered $KHSO_4$ to decompose the soap before distilling.

Free Fatty Acid.—Dissolve or disintegrate 5–10 grams of the grease in 50 cc. of ethyl alcohol (or No. 30 specially denatured alcohol) which has previously been neutralized with phenolphthalein and 0.1 N NaOH. Digest on the water bath until the alcohol beings to boil. Titrate with 0.1 N NaOH until a pink color persists after vigorous shaking. Calculate to oleic acid.

CALCULATION.—1 cc. 0.1 N NaOH = 0.0282 gram oleic acid.

Ash.—Ignite 2 grams in a porcelain crucible, gently at first and finally at a higher heat, until the ash is as nearly white as possible. Cool in a desiccator and weigh.

Soap.—To the ash add a few cc. of water and a drop of methyl orange and titrate with 0.5 N HCl. Test this solution qualitatively for Pb, Ca, K and Na (see also p. 369), and then calculate the titration to the proper soap by using one of the following factors:

1 cc. 0.5 N HCl = 0.161 gram K stearate.
= 0.153 gram Na stearate.
= 0.152 gram Ca stearate.

If the grease contains a Pb soap, the Pb may be determined by decomposing the grease by boiling with a mixture of H_2SO_4 and HNO_3, evaporating to strong fumes of SO_3, cooling, diluting with water and alcohol and weighing as $PbSO_4$ (see p. 276). In the case of a pigmented grease determine the Pb in the ash. ($PbSO_4 \times 2.55 = Pb$ Stearate.)

If a rosin soap is present, the figures obtained by using the above factors will be somewhat low, depending upon the amount of rosin soap present, because of the higher combining weight of abietic acid; but for ordinary purposes they will be sufficiently accurate.

Mineral Matter.—The amount of ash other than the alkalies from the soap may be determined by the difference between the total ash and the alkali found by titration. In this case the alkali should be calculated to K_2CO_3, Na_2CO_3 or $CaCO_3$,* as the case may be.

In the case of greases of type *C*, shake about 5 grams of the grease with ether in a glass cylinder and then centrifuge. Repeat with a fresh portion of ether. This removes free oils and fats. Decant the ethereal solutions through a filter paper which has previously been dried and weighed. Wash twice with ether by decantation. Shake the residue in the cylinder with alcohol and filter through the same filter paper. Wash with alcohol. This removes alcohol-soluble soaps. Transfer all the residue to the filter paper by means of alcohol. Dry the paper and residue at 100° C., cool in a desiccator and weigh. This gives the total amount of pigment.† If graphite is present, ignite the residue

* The lime will be present in the ash as $CaCO_3$ rather than CaO on account of the large amount of organic matter, unless ignited over a blast.

† This figure includes any alcohol-insoluble soaps. If it is desired to correct for these, acidify with dil. HCl and shake out with ether. Filter the ether solution of the combined fatty matter, wash free from acid, evaporate off the ether and weigh the fat. Calculate to the appropriate soap.

in a weighed porcelain crucible and subtract this final residue from the total pigment for the amount of graphitic carbon. In general, however, this last step is unnecessary, as all that is desired is the total amount of graphite.

The above determinations are, as a rule, all that is necessary in an examination of the ordinary types of grease. It may be desirable, however, at times to make further determinations and these are given below:

Unsaponified Oil and Fat.—The unsaponified oil may consist of mineral oil together with unsaponified saponifiable oil or fat. This may be determined by extracting 5–10 grams of the grease with neutral ether. If it is desired to know its nature, the ether extract may be subjected to an examination for saponification number, iodine number, etc. In most cases where grease contains unsaponified saponifiable matter, or free fat, it has been made by a partial saponification of the fat in question; hence the original grease may be saponified directly and the total fatty acids examined.

Unsaponifiable Mineral Oil, etc.—These will be found in the ether extract of the grease, together with the free fat, and the proportions of the two can be ascertained by a determination of the saponification number, or by shaking out with ether after saponification (see p. 340).

Reporting Results.—Under ordinary circumstances report results as follows:

1. Type.
2. Melting point (° F.).
3. Moisture (%).
4. Saponifiable oil (%).
5. Mineral oil (%).
6. Total mineral matter (%).
7. Soap (kind and %).
8. Pigment (% and nature).

Ordinarily the mineral oil is taken "by difference" after adding together items 3, 4, 7 and 8.

NOTE.—For specifications for greases see *Bur. Mines Tech. Paper* 323A, p. 17.

DEGRAS (WOOL GREASE)

General.—The term Degras in its present commercial sense refers to crude or recovered wool grease. It is in no way related to the older types, of a similar name, which are now called French Degras—sometimes Sod Oil.

Crude wool grease contains, besides the grease arising from sheep's wool, an indefinite amount of fatty acids recovered from the soap used in washing the wool and obtained in the same operation to which the wool grease is subjected. It is also the custom in many foreign mills to treat the wash waters, arising from the scouring of cloth or yarn with soapy water, at the same time that the wool scourings are treated. It is obvious that the grease obtained as a result of these methods will in all cases contain some free fatty acid from soap; and in case cloth and yarn waters are mixed before treatment, there will also be a certain further amount of fatty acid. In addition there may be a neutral oil or even a mineral oil which comes from the cloth or yarn scouring. It is apparent, therefore, that no standard composition can be ascribed to degras.

A considerable number of samples from various sources analyzed in this laboratory shows the following range in composition:

	Maximum	Minimum	Average
Water	5.9%	None	1.0%
Fatty acid (as oleic)	47.3%	1.0%	18.4%
Mineral acid (as H_2SO_4)	0.19%	None	0.07%
Saponification number	131	80	105

Water.—Determine water by the Xylol Method described on page 358, using a 20-gram sample.

Free Fatty Acid and Mineral Acid.—Follow the procedures for lubricating oils on page 334.

Saponification Number.—Introduce two 5-gram portions, accurately weighed, into separate pressure flasks; add 50 cc. of 0.5 N alcoholic KOH to each; clamp the stoppers tightly and heat the flasks in a steam or hot water bath for at least 8 hours. Run a blank in a separate pressure flask on 50 cc. of the alcoholic

KOH for the same length of time. Keep the flasks covered with a heavy cloth while heating to prevent accident and do not open them until cold. Titrate the solutions in the flasks when cold with 0.5 N HCl and phenolphthalein. Subtract the number of cc. of acid used to neutralize the excess KOH after saponification from the amount required by the blank, multiply the difference by 28.05 and divide by the weight of sample taken. The result is the Saponification Number.

NOTES.—(1) If the sample contains an appreciable amount of free mineral acid, correct the saponification number above obtained by subtracting 1.1 for each 0.1% of H_2SO_4, and report as "saponification number corrected for mineral acid."

(2) *Qualitative Test for Mineral Oil.*—To the solution after titrating for the saponification number add a small piece of KOH, evaporate nearly to dryness on the steam bath, take up the residue with water, transfer to a separatory funnel and shake out the unsaponifiable matter* with ether. Draw off the ether solution and evaporate off the ether. In the absence of mineral oil the residue should be completely soluble in hot 95% alcohol.

BEESWAX

General.—The common adulterants of beeswax are rosin, paraffin, ceresin, stearic acid, spermaceti, and Japan and carnaüba waxes; while to a less extent are used tallow, starch, sulfur, and mineral fillers. Any appreciable amount of water must also be looked upon as an adulterant.

Preliminary Tests.—As a preliminary test for the detection of adulterants, dissolve a portion of the sample in cold $CHCl_3$. Ceresin, paraffin wax, carnaüba wax, and wool wax are not completely soluble and any considerable quantity may thus be detected qualitatively, as well as starch and mineral matter. It should, however, be borne in mind that bleached white beeswax is not readily soluble in $CHCl_3$. Pure beeswax should also be completely soluble in turpentine.

Specific Gravity.—Melt the wax and drop it by means of a stirring rod upon a moist, cold, porcelain surface in such a manner as to obtain globules of about $\frac{1}{8}$ inch in diameter. Let cool for at least 2 hours, and then place in a glass cylinder of about 200-cc. capacity, and add a mixture of 35 cc. of alcohol and 65 cc. of water. If the globules sink in this mixture, add water; if they

* For the determination of unsaponifiable matter, see page 340.

rise, add alcohol. Add water or alcohol with rapid agitation until the globules neither rise nor sink but remain suspended in the liquid at exactly 15.5° C. Then take the sp. gr. of the liquid at this temperature with the Westphal balance. This gives the sp. gr. of the beeswax at 15.5° C.

Melting Point.—Thinly coat the bulb of an accurate thermometer with the wax and let stand 24 hours. Place the bulb of the thermometer in a large test-tube, holding it in place by a cork stopper grooved on the sides so as to allow free access of air. Immerse the test-tube containing the thermometer in a beaker of warm water and raise the temperature very gradually (1° C. in 2–3 minutes). The temperature at which a transparent drop forms on the end of the thermometer is taken as the melting point.

Iodine Number.—Determine the iodine number by the Wijs method as described on page 310.

Acid Number.—Weigh 8 grams into a 500-cc. Erlenmeyer flask and add 70 cc. of neutral alcohol. Heat on the water bath until the mixture is entirely melted. Then add 1 cc. of phenolphthalein solution and titrate the mixture *quickly* with 0.5 N alcoholic KOH solution, keeping it hot. Calculate the number of milligrams of KOH required to neutralize the free acid in 1 gram of wax.

Calculation.—1 cc. 0.5 N alkali = 28.05 mg. KOH.

Note.—Instead of titrating with 0.5 N alcoholic KOH, the determination may be made with 0.5 N or 0.1 N aqueous KOH. In this case, however, it is necessary to dilute with about 200 cc. of hot neutral alcohol before titrating and to keep this solution hot during titration. In any case the wax must be in a melted state during titration.

Saponification Number.—Saponify about 2 grams of wax (accurately weighed) for at least 3 hours with 25 cc. of 0.5 N alcoholic KOH, as described on page 309. Calculate the saponification number.

Ester Number and Ratio Number.—Subtract the acid number from the saponification number. The difference is the Ester Number. Divide this by the acid number. The quotient is the Ratio Number. For pure beeswax the ratio number lies in the neighborhood of 3.8.

Note.—If the saponification number of the sample is below 92 while the ratio number is normal, then paraffin or ceresin must be present. If the ratio number exceeds 3.8, then adulteration may be suspected with Japan wax, tallow, insect wax, carnaüba wax, or spermaceti. If, however, the acid

number is much below 20, Japan wax is absent. If the ratio number is less than 3.8, stearic acid or rosin may be present.

Moisture.—Determine moisture by the Xylol Method as described on page 358.

Rosin.—Test qualitatively for rosin as follows: Heat 1 gram of wax for a few minutes with 1 cc. of 50% alcohol (alcohol of this strength will not extract stearic acid if present), cool and filter. Evaporate the filtrate to dryness on the water bath and add 5 cc. of acetic anhydride. Heat to boiling, cool thoroughly, and then carefully let 1 drop of conc. H_2SO_4 flow into the solution. Rosin will develop a fugitive violet color.

Fatty Adulterants.—Japan wax and other fatty substances (such as tallow, ceresin, stearic acid, etc.) may be detected by boiling 1 gram with 1.5 grams of borax and 20 cc. of water, whereupon the aqueous solution will become milky or gelatinous when cooled. With pure beeswax it remains clear or becomes but slightly turbid. Carnaüba wax and rosin behave similarly to pure beeswax.

NOTE.—The above determinations are generally sufficient to determine whether a sample is adulterated or not. It must be borne in mind, however, that beeswaxes from different localities vary somewhat in composition, also that the sp. gr. of white bleached beeswax is somewhat higher, whereas the other "constants" may be either raised or lowered according to the method employed in bleaching. Indian beeswax (Ghedda wax) is softer and more plastic than normal beeswax from European and domestic sources. It has a very low acid number, and high ester number, and it is said to be rarely adulterated. Care must be taken not to confuse specimens of this wax (and also Chinese beeswax) with adulterated beeswax.

The following table gives the approximate figures which an unadulterated sample should show:

TABLE XVII—CONSTANTS OF ORDINARY AND INDIAN BEESWAX

	Ordinary Beeswax	Indian Beeswax
Sp. gr. at 15.5° C.	0.958–0.970	0.958–0.970
Melting point	62–67° C.	60–68° C.
Iodine number	8–11	5–11
Saponification number	90–104	76–130
Acid number	17–21	4.5–10
Ester number	73–87	69–123
Ratio number	3.6–3.8	7.4–17.9

In an adulterated sample the following tests will be found useful:

Stearic Acid.—Boil 3 grams of wax for several minutes with 10 cc. of 80% alcohol and let cool to 18–20° C. to form a thick paste. After standing 1 hour, filter into a 200-cc. cylinder and dilute the filtrate with water to about 200 cc. If stearic acid is present, it separates into flakes and collects on the surface. The test is sensitive to 1%. If from 7–8% are present, a thick creamy mixture results. Pure beeswax should show no appreciable deposit after standing 1–2 hours.

Paraffin.—Melt 2–10 grams of wax in a porcelain dish, then add an equal weight of finely powdered KOH. Continue heating for a few minutes with continual stirring. Cool and powder the hard mass and mix the resulting powder with three times as much potash lime (1 part KOH : 2 parts CaO) as wax used. Then introduce this mixture into a thick-walled tube, immerse in an oil bath and heat to about 250° C. for 3–4 hours. After cooling, finely powder the tube with its contents, place the mass in a Soxhlet apparatus and extract with 86° Bé naphtha for several hours. Evaporate off the naphtha, dry the residue at 100° C. and weigh. (Make sure the naphtha itself leaves no residue at 100° C.) By this treatment esters are converted into alcohols and these alcohols on heating with potash lime are in turn converted into the respective acids, while hydrocarbons present are not affected and will extract with the naphtha. Pure beeswax contains naturally 12.5–14% of hydrocarbons and any adulteration with paraffin or allied bodies will increase this percentage.

NOTE.—For further information in regard to analysis of doubtful samples, see Allen and Lewkowitsch.

REFERENCES.—Lewkowitsch: "Chemical Technology and Analysis of Oils, Fats and Waxes," **2**, 751. Allen: "Commercial Organic Analysis," 4th ed., **2**, 242–270. *U. S. Dept. of Agr., Bur. Chem., Bull.* 150, 49.

PARAFFIN WAX

General.—For ordinary white paraffin wax the only necessary determination is the melting point. Yellow waxes and paraffin scale, however, often contain a considerable amount of oil. In reporting results of melting point determinations the method used should be stated. It is customary in the trade to use the Fahrenheit scale.

Melting Point.—Capillary Tube Method.—Take a piece of capillary tubing about 1 inch long, soften the wax in the fingers if necessary and push one end of the tube into it, filling the tube about 0.25 inch from the end. Fasten the tube to a thermometer with a rubber band so that the wax is opposite the bulb. Immerse the thermometer bulb and tube in a beaker of water (it will save time if the water is previously warmed to about 90° F.). Heat slowly with a low flame without stirring and note the temperature at which the wax melts and runs out of the tube.

"English Test."—The English Test gives in reality the solidifying point. Stir the melted wax in a small cup, about 2.5 inches in diameter by about 2 inches deep, until the latent heat given up by the crystallization of the wax arrests the fall of the mercury column momentarily. Take this reading as the melting point.

"American Test."—This gives results about 3° F. higher than the English Test and is determined as follows:

A hemispherical cup, 3.75 inches in diameter, is $\frac{3}{4}$ filled with melted wax, which is allowed to cool without stirring until a thin film forms on the top and extends from the sides to a thermometer with a round bulb, 0.5 inch in diameter, suspended so that the bulb is $\frac{3}{4}$ immersed in the center of the cup.

Note.—As the American Test is slow, it is sometimes customary to take the English Test and add 3° F. for the American.

Oil.—Chill the wax and powder it as finely as possible. Weigh out about 1 gram and digest for 1–2 hours in 10 cc. of acetone at ordinary temperature. Mix well, then place in a freezing bath and cool to −15° C. (5° F.) or lower. Filter through cotton wool in a funnel surrounded by a freezing mixture and wash with acetone which has been well chilled. Evaporate the filtrate, dry at not over 100° C. and weigh the oil.

References.—*J. Soc. Chem. Ind.*, **25**, 139 (1906); Rogers-Aubert: "Industrial Chemistry," 527 (1912). See also American Society for Testing Materials, Standard D87–22.

SOAP

General.—Soaps used for washing purposes are the alkali salts of fatty acids. They always contain more or less water and small amounts of impurities incidental to manufacture. In com-

TABLE XVIII—COMPOSITION OF TYPICAL SOAPS

(The figures are maximum percentages unless otherwise indicated)

Kind of Soap	Milled Toilet	Chip	Shaving[1]	White Floating	Ordinary Laundry	Salt Water	Automobile	Hand Grit	Scouring
Nature of Fat	Tallow, 87 % Cocoanut-oil, 13 %	Mixed Fats	Tallow and Cocoanut	Tallow Plus 25 30 % Cocoanut	Mixed Fats; Some Rosin	Pure Cocoanut	Vegetable Oils		
Moisture and volatile matter	15	15	15	34	36	55	55	15	5
Free NaOH	0.1	0.5	0.05[4]	0.15	0.5	0.5	0.05	0.1	0.1
Free oleic acid	.....	.....	.....	....	...	....	0.1	.....	.....
NaCl	0.3	1	0.3[4]	1	1.5	2.5–3.5	....	.....	.....
Insoluble in alcohol[2]	0.3	1.5	0.3[4]	1	1–8	2–3	0.5	0.3[5]	3[5]
Insoluble in water	0.1	0.2	0.1	0.2	1	0.5	0.1	30–35	75–93
Unsaponified fat	0.1	.....	0.1	....	...	....	1–4	.....	.....
Rosin	None	None	None	None	25	None	None	None	None
Sodium silicate	0.15	.....	.....	....	...	....	....	.....	.....
Mixed fatty acids:									
Acid number	203–212	....	190–215	212[3]	...	250[3]	....	.....	.....
Titer test[3]	37° C.	39° C.	40° C.	....	...	....	....	.....	.....

[1] About 50 % of the total alkali should be K_2O.

[2] Essentially free carbonate.

[3] Minimum.

[4] Calculated as the K salt.

[5] Free Na_2CO_3 or $Na_2Si_4O_9$.

mercial soaps certain other substances are often present, such as rosin, as a substitute for part of the fats; sodium carbonate, borax, and other salts for increasing hardness and detergency; sand, pumice, etc., for scouring; and cheapening fillers, such as mineral oil, wax, sodium silicate, talc, etc. Hard soaps are made from soda or a mixture of soda and potash, whereas soft soaps are potash soaps (unless the softness is merely caused by an excess of water). The potash soaps are more easily soluble. Liquid soaps are usually water solutions of a neutral cocoanut-oil potash soap, containing glycerol, alcohol, or sugar to prevent cloudiness and foaming.

There are three general methods of soap making:

(*a*) The Boiling process, where the fats are boiled with the alkali and the resulting soap separated from most of the liquid which contains the glycerol and impurities. This allows recovery of glycerol.

(*b*) The Cold process, where the melted fat is mixed with conc. alkali and no outside heat is used.

(*c*) The Half-boiling process, which is similar to (*b*) except that the ingredients are mixed hot. In this process, as well as in (*b*), there is no separation of the soap from the liquid and it contains all the glycerol and impurities. It also frequently contains unsaponified fat.

The general composition of some typical soaps is indicated in Table XVIII, most of the data being taken from government specifications.

The following procedures cover the analyses of (*a*) ordinary solid soaps, hard or soft; (*b*) scouring soaps; (*c*) liquid soaps.

Solid Soaps

Preparation of Sample.—The preparation of the sample requires considerable care, since the moisture content of the outer layer may be very different from that of the interior of the cake.

If the sample is comparatively dry, it is well to run it through a meat chopper and reduce to fine particles, repeating the operation several times in order to obtain a homogeneous sample. If the soap is too soft to permit this procedure, cut the cake in two diagonally, and take thin shavings from fresh surfaces, being careful to cut entirely across in order to obtain a fair proportion

of the outer and inner parts. The sample in either case should be thoroughly mixed and kept in a tightly stoppered bottle. Samples for analysis should be weighed out as soon as possible.

Moisture and Volatile Matter.—Weigh out 20 grams of the sample and dissolve in about 150 cc. of hot water. Transfer the solution while still hot to a 250-cc. volumetric flask and dilute to the mark. Mix thoroughly, pipette 25 cc. of the hot solution immediately* into a weighed platinum dish and evaporate to dryness on the steam bath. Then dry to constant weight at not over 105° C. The percentage of solid matter subtracted from 100 gives the percentage of moisture and volatile matter.

NOTES.—(1) The loss as determined above may also include alcohol and essential oils, if they are present in the soap; also naphtha or other volatile substances. In such cases the true moisture may be determined by the Xylol Method, page 358, using about 20 grams of soap and acidifying with an excess of powdered anhydrous $KHSO_4$ before distilling.

(2) For the most accurate work the drying should be conducted *in vacuo* or in an inert atmosphere.

Total Alkali.—METHOD I.—Ignite the residue from the moisture determination at a low red heat until all carbonaceous matter is burned off. Weigh the mineral residue, which consists of Na_2CO_3 or K_2CO_3 (also SiO_2, NaCl, etc., if present). Pour boiling water into the dish and warm until the residue is dissolved. Cool, and titrate with 0.1 N acid and methyl orange. If the residue is not completely soluble in water, the insoluble matter should be filtered off and the filtrate evaporated to dryness, ignited, and weighed before titration.

The alkali by titration, calculated either to Na_2CO_3 or K_2CO_3, should check with the weight of soluble ash as above determined. If it does not, the presence of both Na and K is indicated (provided NaCl, etc., are absent). To confirm the presence of both elements, take an amount of ash the size of a pinhead, dissolve in a few drops of HCl, put 1 drop on a microscope slide, evaporate to dryness over a micro burner, and draw across it with a glass rod a drop of saturated uranium acetate solution made slightly acid with acetic acid. If Na is present, clear-cut, light-yellow tetrahedra of sodium uranium acetate will appear. Put another

* If the total fatty matter is to be determined, pipette the 200-cc. aliquot for that determination also before the solution is allowed to cool.

small drop on a slide and run in from the side a smaller drop of H_2PtCl_6 solution. Potassium will give yellow octahedra.

CALCULATIONS.—1 cc. 0.1 N acid = 0.005300 gram Na_2CO_3.
= 0.006910 gram K_2CO_3.
= 0.003100 gram Na_2O.
= 0.004710 gram K_2O.

$$Na_2CO_3 \times 0.5849 = Na_2O.$$
$$K_2CO_3 \times 0.6816 = K_2O.$$

METHOD II.—The following method is more convenient when it is not necessary to determine total fat. Dissolve 5 grams of the soap in 100—150 cc. of hot water. Add 40 cc. of 0.5 N HCl. Heat on the steam bath until the fatty acids have collected in a clear layer. Cool by placing the beaker in cold water, break the cake of fatty acids and filter the aqueous liquid, leaving as much of the fatty acids as possible in the beaker. Thoroughly wash the beaker, fatty acids and filter paper with water, unite the filtrate and washings, add methyl orange and titrate the excess of acid with 0.1 N NaOH. Calculate the amount of 0.5 N acid consumed in terms of Na_2O or K_2O.

Total Fatty Matter.—Pipette 200 cc. of the original hot soap solution (see Moisture) into a beaker,* add dil. HNO_3 until slightly acid, heat on the water bath until the fatty acids have collected in a clear layer on top and the solution below is perfectly clear. Cool in ice water or let stand overnight. Remove the layer of fatty acids to a beaker. Shake out the remaining liquid in a separatory funnel with 2 portions of 50 cc. each of $CHCl_3$ to remove the rest of the fatty matter. Transfer the $CHCl_3$ extract to the beaker containing the fatty cake and dissolve the latter. Transfer the $CHCl_3$ solution to a separatory funnel, rinsing the beaker with $CHCl_3$. Wash the $CHCl_3$ extract with 2 portions of 20 cc. of water. Evaporate off the $CHCl_3$, dry at 100°C. to constant weight and weigh as Total Fatty Matter.

NOTES.—(1) The fatty matter is determined above as fatty acids, whereas it exists in the soap as anhydrides, which for ordinary soap materials equals acids $\times$ 0.9673.† Usually analyses are reported giving the total

* Time may be saved, if necessary, by pipetting directly into the separatory funnel; then acidify, and shake thoroughly before adding $CHCl_3$.

† Lewkowitsch: "Chemical Technology and Analysis of Oils, Fats and Waxes," 624 (1895).

fatty matter as fatty acids, since small losses are almost inevitable in this determination and for commercial analyses the direct figure obtained is usually the most satisfactory.

(2) The total fatty matter as determined may include fatty acids, uncombined fat, rosin, and hydrocarbons. If it is desired to determine only the combined acids, the determination should be made on a portion of the dry soap previously extracted with ether or 86° Bé gasoline, as described later under Total Unsaponified Matter.

(3) If the fatty acids are liquid at ordinary temperature, a known weight of beeswax or stearic acid may be added to the hot liquid before chilling to form a solid cake. The weight of wax added should be about equal to that of soap employed and should be deducted of course from the weight of the cake. Excess of water may be removed by pressing between filters, the cake dried in a desiccator (or *in vacuo*) and weighed.

(4) Cocoanut and palmnut oil soaps yield a fatty acid soluble to a slight extent in hot water. In such cases the separation of fatty acids should be made in as concentrated a solution as possible, saturated with common salt. The washing of the fatty acids should be limited and drying carried on with as little exposure to heat as possible.

(5) If it is necessary to determine the soluble fatty acids, consult Allen's "Commercial Organic Analysis," 4th ed., **2,** 432.

Free Caustic Alkali or Free Fatty Acids.—Dissolve 5 grams of soap in hot 95% alcohol which has been freshly neutralized to phenolphthalein with 0.1 or 0.5 N NaOH. Filter, using a hot-water funnel;* wash free from soap with hot neutral alcohol; titrate the filtrate with 0.1 N acid and phenolphthalein and calculate to NaOH or KOH, as the case may be.

If the filtrate is acid, titrate with 0.1 N NaOH and calculate to oleic acid.

CALCULATION.—1 cc. 0.1 N acid = 0.00400 gram NaOH.
= 0.00561 gram KOH.
1 cc. 0.1 N NaOH = 0.0282 gram oleic acid.

NOTES.—(1) The presence of free caustic alkali may be detected by treating a freshly cut surface of the soap with a few drops of phenolphthalein solution. If no red coloration appears, it may be assumed that free caustic alkali is absent. Either free caustic or sodium silicate will give a bright red coloration. In the presence of excess moisture, however, Na_2CO_3 will also give this color.

(2) If the soap contains both free alkali and free fat, the above method is open to objection, since during heating with alcohol the free alkali will saponify some of the free fat. In cases where great accuracy is required, Devine's method should be used. For details see *J. Am. Chem. Soc.*, **22,** 693.

* See also Insoluble in Alcohol and Insoluble in Water.

Insoluble in Alcohol.—If it is desired to determine the amount of material insoluble in alcohol, make the filtration of the alcoholic solution in the Free Caustic Alkali determination on a tared filter paper or a weighed Gooch crucible; dry at 100–105° C. for 3 hours, cool in a desiccator and weigh.

Free Sodium Carbonate.—Dissolve the residue from the alcoholic solution in the above determination by pouring boiling water through the filter. Wash, cool the solution, and titrate with 0.1 N acid and methyl orange. Calculate to Na_2CO_3 or K_2CO_3, as the case may be. (It is well to test the residue in a flame with a platinum wire before dissolving it.)

CALCULATION.—1 cc. 0.1 N acid = 0.005300 gram Na_2CO_3.
= 0.006910 gram K_2CO_3.

NOTE.—If borax or sodium silicate is present, it is sufficiently accurate for commercial purposes to assume that they will remain insoluble in alcohol and be titrated with the free carbonate. In this case corrections should be made on the methyl orange titration of carbonate as follows:

1 cc. 0.1 N acid = 0.013 gram $Na_2Si_4O_9$.*
= 0.0191 gram $Na_2B_4O_7 \cdot 10HO$.

Insoluble in Water.—If the amount of material insoluble in water is desired, proceed as in the determination of Insoluble in Alcohol and wash the residue thoroughly with water at 60° C. (If the matter insoluble in water is all inorganic, boiling water may be used as under Free Sodium Carbonate.) Dry the insoluble residue for 3 hours at 100–105° C., cool in a desiccator and weigh.

Combined Alkali (Na_2O or K_2O).—Calculate the free caustic and free carbonate to Na_2O or K_2O and deduct from the total alkali calculated as NaO or K_2O_2. The difference will be the combined alkali (provided sodium silicate and borax are absent).

CALCULATIONS.—$NaOH \times 0.7748 = Na_2O$.
$KOH \times 0.8394 = K_2O$.
$Na_2CO_3 \times 0.5849 = Na_2O$
$K_2CO_3 \times 0.6816 = K_2O$.

Sodium Silicate.—The presence of sodium silicate is generally indicated by the fact that the weight of the ash is appreciably

* Theoretically, 1 cc. of 0.1 N acid = 0.01511 gram $Na_2Si_4O_9$, but commercial silicate varies somewhat in composition and 0.013 is taken as being nearer the actual average titration

greater than the weight calculated from the titration (provided, of course, that insoluble abrasives are not present). The amount of sodium silicate may be ascertained by determining SiO_2 in the ash after titration for total alkali. Add a slight excess of HCl, evaporate to dryness, and bake for 1 hour at 130° C. Take up with HCl, dilute with hot water, filter, wash, ignite very strongly and weigh as SiO_2. Calculate to $Na_2Si_4O_9$.

CALCULATION.—$SiO_2 \times 1.258 = Na_2Si_4O_9$.

NOTE.—If the soap contains insoluble silicious matter, make a water solution, filter, evaporate the filtrate, burn off the organic matter, and determine SiO_2 as above directed.

Borax.—Weigh 10 grams of soap (or 5 grams, if more than 5% of borax is suspected) into a platinum dish and add 2.15 grams of a fusion mixture consisting of 200 grams of Na_2CO_3 and 15 grams of SiO_2 finely powdered. Then add 15 cc. of alcohol, mix with the aid of a glass rod, and, after washing the rod with a little alcohol, evaporate the mass to dryness on the water bath. Ignite until combustible material is destroyed, cover the dish with a piece of platinum foil and fuse. Completely disintegrate the fusion by boiling with water and transfer the solution to a 250-cc., round-bottomed flask. Acidify with 20 cc. of dil. HCl (1:1). Heat nearly to boiling and add a moderate excess of dry precipitated $CaCO_3$. Connect with a reflux condenser and boil vigorously. Filter out the precipitate through a folded filter, and wash several times with hot water, keeping the total volume of liquid below 100 cc. Return the filtrate to the flask, add a pinch of $CaCO_3$ and again boil under the reflux condenser. Remove the flame and connect the top of the condenser with a suction pump. Apply suction until boiling has nearly ceased, cool to ordinary temperature, add 1 gram of mannite or 50 cc. of neutral glycerol,* and titrate the solution with 0.1 N NaOH (free from carbonate) and phenolphthalein. After the end-point is reached, add 1 gram more of mannite or 10 cc. more of neutral glycerol and again titrate. Repeat this process until the addition of mannite or glycerol causes no further action on the end-point. Calculate the titration to crystallized borax.

CALCULATION.—1 cc. 0.1 N NaOH = 0.00954 gram $Na_2B_4O_7 \cdot 10H_2O$.

* Mannite gives a sharper end-point than glycerol.

NOTES.—(1) This method is described in *J. Ind. Eng. Chem.*, **5**, 645 (1913).

(2) It is always advisable to test the soap qualitatively before undertaking a quantitative determination.

Qualitative Test for Borax.—Place about 1 gram of the soap in a test-tube with 10 cc. of dil. HCl. Heat the mixture to boiling, which causes the fatty acids to rise to the surface. Cool under the tap and filter through a wet filter paper. Immerse a strip of turmeric paper in the mixture and dry it. If borax is present, the paper will acquire a deep red color when dry and this color will change to blue or green when treated with NH_4OH or Na_2CO_3 solution. The test is sensitive to about 0.05% of borax in the soap.

Chlorides (Salt).—METHOD I.—Evaporate the filtrate from the fatty acids, separated by HNO_3, to about 100 cc. Neutralize carefully with $CaCO_3$, and titrate with 0.1 N $AgNO_3$, using K_2CrO_4 as indicator (see p. 687).

CALCULATION.—1 cc. 0.1 N $AgNO_3$ = 0.00585 gram NaCl.
= 0.00746 gram KCl.

METHOD II.—Dissolve 5 grams of the soap in 300 cc. of water. Boil if necessary to get all soluble matter into solution. Add an excess of neutral chlorine-free $Mg(NO_3)_2$ solution. About 25 cc. of a 20% solution is usually sufficient. Without cooling or filtering, titrate as above with 0.1 N $AgNO_3$ solution, using K_2CrO_4 indicator.

Glycerol.—Dissolve 20–25 grams of soap in hot water, add a slight excess of H_2SO_4 and heat on the water bath until the fatty acids separate in a clear layer. Remove the fatty acids and filter the acid solution into a volumetric flask. Remove chlorides and soluble fatty acids by adding crystals of Ag_2SO_4. Cool, make up to the mark, mix, let settle and filter through a dry filter paper. Place an aliquot portion corresponding to about 5 grams of soap in a 100-cc. volumetric flask, dilute slightly, add a little silver oxide, let stand 10 minutes, and add a slight excess of basic lead acetate. Make up to the mark, filter through a dry paper, and place 25 cc. of the filtrate in a perfectly clean beaker. Add first 12 drops of dil H_2SO_4 (1:4) to precipitate the Pb, and then an accurately measured amount (40–50 cc.) of a solution of bichro-

mate (made by dissolving 74.56 grams of pure $K_2Cr_2O_7$ in water and diluting to 1000 cc., the exact strength then being determined against pure iron or ferrous ammonium sulfate), and then 15 cc. of conc. H_2SO_4. Cover the beaker and heat for 2 hours in boiling water; then cool. Add an excess of standard ferrous ammonium sulfate solution and titrate back with standard bichromate solution containing 7.456 grams per liter. (The ferrous ammonium sulfate solution should contain about 240 grams per liter.) 1 cc. of the *stronger* bichromate solution corresponds to 0.01 gram of glycerol.

In the presence of sugar the above method is not reliable, since sugar will also reduce bichromate. Consequently, when sugar is present, remove the fatty acids as before, neutralize an aliquot with milk of lime, evaporate to about 10 cc., add 2 grams of sand and milk of lime containing about 2 grams of $Ca(OH)_2$, and evaporate almost to dryness. Treat the moist residue with 5 cc. of 95% alcohol, rub the whole mass into a paste, heat the mixture on the water bath, stirring constantly, and decant the liquid into a 250-cc. volumetric flask. Wash the residue five or six times with small portions of alcohol, adding the washings to the flask. Cool the contents of the flask to 15° C., fill to the mark with 95% alcohol, mix, and filter through a dry paper. Evaporate 200 cc. of the filtrate to a syrupy consistency on the water bath, transfer to a stoppered cylinder with 20 cc. of absolute alcohol, add 3 portions of 10 cc. each of absolute ether, mixing after each addition; let stand until clear, pour off through a filter, and wash the contents of the cylinder on the filter with a mixture of 2 parts of absolute alcohol and 3 parts of absolute ether. Evaporate to a syrup; dry for 1 hour at the temperature of boiling water, weigh, ignite, and weigh again. The loss multiplied by 1.25 is the weight of glycerol in the aliquot taken. (Instead of weighing the glycerol it may be titrated with bichromate after driving off the alcohol and ether.)

NOTE.—According to Hoyt and Pemberton,* by using the proper amounts of $K_2Cr_2O_7$ and H_2SO_4 in excess both the glycerol and the sugar can be completely reduced. The amount of $K_2Cr_2O_7$ consumed by the sugar can be calculated from a separate determination of the sugar and then the glycerol calculated from the difference.

* *J. Ind. Eng. Chem.*, **14**, 54 (1922).

Sugar.—Dissolve 5 grams of soap in water, add an excess of HCl, and heat on the steam bath for 30 minutes. Cool and filter out the fatty acids, collecting the filtrate in a volumetric flask. Nearly neutralize the excess of acid with NaOH, make up to volume and mix. For analysis take an aliquot depending upon the amount of sugar supposed to be present. The aliquot must not contain more than 0.25 gram of sugar calculated as dextrose. Determine the total reducing sugars by Allihn's modification of Fehling's method (see p. 556) and calculate as dextrose.

Cane sugar = dextrose $\times$ 0.95.

NOTE.—Sugar is often found in transparent toilet soaps, especially those sold as "glycerin soaps," to the extent of 20–30%. Such soaps also often contain alcohol and sodium acetate.

Total Unsaponified Matter.—METHOD I.—Dry 10 grams of soap and extract in a Soxhlet extractor* with absolute ether or naphtha (boiling below 60° C.). Transfer the extract to a separatory funnel and wash twice with water. Evaporate off the solvent, dry at 100–105° C. and weigh.

METHOD II.—Dissolve 10 grams in about 200 cc. of water. Extract in a separatory funnel with 2 portions of 100 cc. each of ether. After shaking with the ether add a few cc. of alcohol and give the funnel a whirling motion to obtain a clear solution. Combine the ether extracts, wash twice with water, evaporate off the ether and weigh the unsaponified matter.

Unsaponifiable Matter.—To the total unsaponified matter as determined above add 25 cc. of approximately 0.5 N alcoholic KOH, boil under a reflux condenser for 1 hour, evaporate to dryness, dissolve in water, transfer to a separatory funnel, shake out with ether, wash the ether free from alkali, evaporate off the ether in a weighed dish or flask, dry at 100° C. and weigh.

NOTE.—The unsaponifiable matter thus obtained is the natural unsaponifiable matter of the oils or fats together with any wax or heavy petroleum hydrocarbons non-volatile with steam.

Unsaponified Saponifiable Matter.—Subtract the unsaponifiable matter from the total unsaponified matter.

* A convenient way to do this is to dissolve the soap in a small amount of hot water and pour it slowly upon a layer of ether-extracted sand in a flat-bottomed evaporating dish. Then evaporate on the steam bath and finally dry at 105° C. and transfer to the extractor.

Naphtha.—For the determination of naphtha or other hydrocarbons volatile with steam, place in a liter round-bottomed wide-neck flask about 400 cc. of water and add about 50 cc. of dil. H_2SO_4 (1 : 1). After cooling the solution, if necessary, introduce about 100 grams of soap, weighed to 0.1 gram, into the flask. The soap should be weighed as one piece and cut quickly into as large pieces as will go through the neck. Then introduce into the neck of the flask a 2-hole rubber stopper connecting through one hole by a bent glass tube to a condenser. Through the other hole run a glass tube nearly to the bottom of the flask. This tube is for admission of steam. Connect the outlet of the condenser by means of an adapter to a long tube graduated to 0.1 cc. A gas burette with a good-sized bulb at the bottom is satisfactory. By means of a rubber tube connected to the bottom of this burette water can be drawn off as it accumulates without disturbing the upper layer of naphtha. Surround the graduated tube with ice water. Heat the solution in the flask to boiling and then pass in steam. Continue the steam distillation until the condensate comes over perfectly clear. This generally requires 1–2 hours. Have sufficient water in the measuring tube so that the upper layer of naphtha remains in the graduated portion, carefully drawing off the underlying water as fast as necessary.

After completing the distillation, let the contents of the tube come to 60° F. and read the volume of the upper layer. Then determine the sp. gr. at 60° F. of the volatile distillate. From this calculate its weight. Transfer the entire volatile distillate to an Erlenmeyer flask. Add 25 cc. of alcohol which has been neutralized (hot) to phenolphthalein, warm on the steam bath about 15 minutes and titrate with 0.1 N NaOH and phenolphthalein. This gives the fatty acids volatile with steam. Calculate the total weight of fatty acids as oleic acid and subtract from the weight of the volatile distillate. Figure the difference to percentage of naphtha by weight.

Calculation.—1 cc. 0.1 N NaOH = 0.028 gram oleic acid.

Note.—If the volatile fatty acids amount to more than a few tenths of a per cent, it is more accurate to redistill the first steam distillate by means of steam after adding a liberal excess of 10% NaOH solution to neutralize the fatty acids, collecting the distillate as before in a graduated tube surrounded by ice water.

Examination of Fatty Acids.—(*a*) Separation and Preparation.—*Method I* (*for Ordinary Soaps*).—Dissolve about 50 grams of the soap in 500 cc. of hot water, add 100 cc. of 30% H_2SO_4, heat until the fatty matter collects in a clear layer, draw off the acid layer and wash the fatty matter free from H_2SO_4 with hot water. Decant the fatty matter into a dry beaker, filter through a hot-water funnel and dry for 20 minutes at the temperature of boiling water.

Method II (*for Toilet Soaps and Soaps Containing Volatile Fatty Acids*).—Dissolve about 50 grams of the soap in 300 cc. of hot water, transfer to a separatory funnel and add 150 cc. of approximately 2 N H_2SO_4. Cool somewhat, add 120 cc. of ether, shake, draw off the acid layer and wash the ether layer free from acid with strong NaCl solution. Draw off the aqueous layer as completely as possible, transfer the ether layer to a flask, add 20–30 grams of anhydrous Na_2SO_4, stopper the flask, shake and let stand at a temperature below 25° C. until the ethereal liquid becomes perfectly clear, indicating that the Na_2SO_4 has absorbed all the water. Filter through a dry paper into another Erlenmeyer flask and completely evaporate off the ether by passing through the flask a current of dry air and heating the flask to a temperature not above 50° C.

(*b*) Titer Test.—See page 312.

(*c*) Acid Number.—See page 311.

Rosin.—(*a*) Twichell Method.—Dissolve 3 grams of the separated and dried fatty acids in 30 cc. of absolute alcohol in a flask and pass dry HCl gas through the solution in a moderate stream. Keep the flask cool by placing it in a vessel of cold water. Continue passing the gas until the esters separate and no more HCl is absorbed, which usually requires about 45 minutes. Let the flask stand about 1 hour until the acid solution is clear and the esters containing the rosin float on top. Transfer to a separatory funnel, wash the flask out with 50 cc. of gasoline (about 74° Bé). Run off the acid solution, wash the gasoline solution once with water, treat with a solution of 0.5 gram of KOH and 5 cc. of alcohol in 50 cc. of water, and shake. Rosin is immediately saponified and 2 layers will separate completely. Draw off the lower solution of rosin soap into another separatory funnel, acidify with dilute acid and shake out three times with ether.

Wash the combined ether extract twice with water, draw into a weighed flask, evaporate off the ether, dry the rosin at 100° C. and weigh.

NOTE.—The above method is described in *J. Soc. Chem. Ind.*, 804 (1891), and depends upon the fact that aliphatic acids are converted into ethylic esters by HCl in alcoholic solution, whereas rosin remains unchanged.

(*b*) WOLFF METHOD.*—Dissolve 5 grams of soap in 100–200 cc. of hot water, add a slight excess of dil. H_2SO_4, heat until the fatty acids collect in a clear layer, cool to room temperature, extract with a small amount of ether, draw off the aqueous layer and wash the ether solution free from mineral acid with water. Transfer to a 200-cc. Erlenmeyer flask, evaporate off the ether and dry for 1 hour at 105° C. Cool and dissolve in 20 cc. of absolute alcohol. Then add 10 cc. of a mixture of 1 volume of conc. H_2SO_4 and 4 volumes of absolute alcohol and boil 4 minutes under a reflux condenser. Remove from the steam bath and add to the liquid about five times its volume of NaCl solution (7–10%). Shake out the aqueous solution with 3 portions of ether, combine the ether solutions and wash with NaCl solution until the washings are neutral to methyl orange. Add 30 cc. of alcohol neutral to phenolphthalein and titrate the rosin acids with 0.1 N NaOH and phenolphthalein.

CALCULATION.—1 cc. 0.1 N NaOH = 0.0346 gram rosin.
= 0.0377 gram Na resinate.

Miscellaneous Substances.—Metallic substances such as Pb, Hg, Cu, and Zn will be found in the filtrate from the SiO_2 determination and may be determined by the usual methods.

Dextrin, starch, gelatin, etc., are sometimes present in soap and they may best be determined in aliquot portions of the filtrate from the total fatty matter. In this case, however, H_2SO_4 or HCl should be used in place of HNO_3 to separate the fat.

Carbolic acid and coal tar products may be determined by the method described in Allen's "Commercial Organic Analysis," 4th ed., **2,** page 426.

SCOURING SOAP

General.—The methods for scouring soaps are similar to those given above, with the following exceptions:

* *Bur. Standards, Circ.* 129.

Insoluble Siliceous Material.—In the case of scouring soaps the material insoluble in water should be reported as Insoluble Siliceous Material.

Feldspar and Quartz.—The approximate amount of feldspar contained in the abrasive material of scouring soap (when it is known to contain nothing but feldspar or quartz or a mixture of the two) may be determined by decomposing about 0.5 gram of the abrasive material with HF, taking up the residue in water and HCl and determining the Al_2O_3 by precipitation with NH_4OH. This weight, multiplied by 5.48 and divided by the weight of sample, gives the approximate percentage of feldspar in the abrasive material.

Total Alkali.—The total alkali should be determined by Method II as previously given and not by titrating the ash, since the alkali of the soap will fuse the mineral silicate when the material is ashed.

Liquid Soap

General.—Except as indicated below, the methods of analysis for liquid soaps are similar to those for hard soaps, bearing in mind that the liquid soaps contain a large amount of water.

Total Anhydrous Soap and Alkali Combined as Soap.*—Dissolve 10 grams of the sample in 100 cc. of water in a 250-cc. Erlenmeyer flask. Add a slight measured excess of 0.5 N HCl, insert a small funnel in the neck of the flask and heat at a temperature not exceeding 60° C. until the fatty acids separate as a clear layer. Transfer to a separatory funnel, draw off the acid layer into a second separatory funnel, and shake the acid aqueous liquid with two 20-cc. portions of ether. Dissolve the fatty acids in the ether used for washing the aqueous liquid and shake with 10-cc. portions of water until no longer acid to methyl orange. Unite the water portions used for washing and shake with 20 cc. of ether, washing this ether until the wash water is neutral to methyl orange. Unite the ether solutions (filter if necessary, washing the paper with ether) in a suitable weighed vessel. Add 100 cc. of neutral alcohol, free from CO_2, and titrate to exact neutrality to phenolphthalein with standard KOH solution. Evaporate off the alcohol, dry to constant weight at 105° C., weigh as K soap, and calculate the percentage.

* *Bur. Standards, Circ.* 124.

The soap thus formed includes any mineral oil and neutral fat which, if determined separately, must be deducted from the result to obtain the true soap. Calculate from the amount of standard KOH the amount of K_2O (combined as soap) added and deduct this from the weight of K soap to obtain the fatty anhydrides.

NOTES.—(1) Liquid soaps are generally solutions of potash soap. If the soap is known to be a soda soap, the fatty acids may be titrated with NaOH instead of KOH, or the proper correction may be made by calculation.

(2) If the sample shows an excess of free fatty acid, proper corrections must be made in calculating the combined alkali in the original soap.

(3) A blank test should be made on the standard caustic solution for neutral salts and the proper corrections made if necessary.

Free Carbonate Alkali.—Warm together all the acid aqueous liquids from the determination of Total Anhydrous Soap to drive off dissolved ether. Cool, add methyl orange, and titrate the excess acid with 0.5 N caustic for the amount of acid consumed by the sample. Calculate the total alkali as K_2O. Subtract the amount of K_2O combined as soap and as free KOH and calculate the difference to K_2CO_3.

CALCULATIONS.—1 cc. 0.5 N acid = 0.02355 gram K_2O.

$$KOH \times 0.8394 = K_2O.$$

$$K_2O \times 1.4671 = K_2CO_3.$$

Free Caustic Alkali or Free Fatty Acid.—Digest hot 10 grams of the sample with 200 cc. of freshly boiled, neutral ethyl alcohol (94% or stronger). Filter and wash the precipitate with freshly boiled, hot, neutral alcohol until free from soap; unite the filtrate and washings, add phenolphthalein and titrate with 0.1 N HCl or NaOH. Calculate the percentage of free caustic as KOH or of free acid as oleic acid.

SOAP POWDERS AND SCOURING COMPOUNDS

Soap powders are generally mixtures of powdered soap with soda ash (Na_2CO_3), "monohydrate" ($Na_2CO_3 \cdot H_2O$), or sal soda ($Na_2CO_3 \cdot 10H_2O$). Sometimes part of the alkali is replaced by $NaHCO_3$, borax, or Na_3PO_4; and some of the "stronger" and less desirable powders contain NaOH. Scouring compounds also contain an insoluble abrasive such as pumice, feldspar, etc. or a "carrier" like corn meal.

The methods of analysis are similar to those for soap. If the sample contains insoluble matter, treat 10–20 grams with hot water, filter through a tared filter or Gooch crucible and wash with hot water, collecting the filtrate in a volumetric flask. Dry and weigh the residue; then ignite and again weigh.

Make the filtrate up to volume. Evaporate an aliquot representing $\frac{1}{10}$ of the total to dryness, ignite and weigh the ash. Dissolve it in water and titrate for total alkali with 0.5 N acid. Determine the fat in another aliquot representing $\frac{4}{5}$ of the sample. Determine moisture on 2–5 grams of the original sample, then determine free alkali on this same portion as described under Soap, titrating with 0.5 N or N acid.

If the sample does not contain insoluble matter, determine the fat directly on a 20-gram portion; moisture, ash, and total alkali on a 2-gram portion; and free alkali on another 2-gram portion.

If it is desired to determine merely the proportions of anhydrous soap and alkali, extract 5 grams in a thimble in a Soxhlet extractor with neutral alcohol, or dissolve in about 200 cc. of neutral alcohol, freshly boiled, filter and wash with hot, freshly boiled, neutral alcohol. Add to the alcoholic solution 2 or 3 drops of phenolphthalein solution. If free caustic is present, titrate it with 0.1 N HCl. Evaporate the alcohol and weigh the dry soap, correcting for the NaCl formed from the 0.1 N HCl added. (1 cc. 0.1 N HCl = 0.0058 gram NaCl.)

The free carbonate, etc. is left in the thimble or on the filter. Dissolve it in hot water, cool, and titrate with 0.5 N or N HCl and methyl orange.

CHAPTER VIII

ANALYSIS OF WOOD, PAPER, AND PAPER-MAKING MATERIALS

CELLULOSE IN WOOD

Sampling.—Samples are best obtained from green wood. If the wood is dry it should be soaked in water. Place the wood in a vise and rasp across the grain with a woodworker's rasp, with the object of obtaining the sample in as fibrous a condition as possible, like mechanical pulp. Dry the rasped wood at 98–100° C.

Total Cellulose.—Weigh out samples of 5 grams each into 500-cc. casseroles. Add 200 cc. of 1% NaOH solution to the fiber, cover with a watch glass and boil gently for 0.5 hour, washing the fiber down from the sides of the vessel several times. Filter with suction on a 1-inch perforated plate placed in a 5-inch funnel. A little of the fiber will run through the plate at first and must be poured back after a good mat, like an asbestos filter, is formed. In order to hold the plate firmly in the funnel during filtration and the subsequent manipulations, pass a piece of fairly stiff silver wire up through one of the holes in the center of the plate and securely fasten it by bending the end down. Let the silver wire extend down through the stem of the funnel, projecting $\frac{1}{8}$ inch beyond the end. By putting one or two slight bends in this wire it can be made to bear against the inside walls of the stem, holding the filter plate firmly in place.

Wash the boiled wood with a good volume of hot water, suck dry, loosen up the fiber with a sharp-pointed glass rod, and attach the stem of the funnel to the rubber tube leading from a chlorine generator under a good hood. Cover the funnel with a watch glass and pass a stream of washed chlorine gas up through the fiber at the rate of 1–2 bubbles per second. Continue the chlorination for 1 hour. Loosen the fiber every 15 minutes and break up the lumps with the pointed rod.

After chlorination return the funnel to the suction flask and wash with hot water to remove HCl. Place 150 cc. of 2% Na_2SO_3 solution in a wash bottle. Invert the funnel over a 500-cc. casserole, push on the silver wire until the main mass of the fiber with the filter plate drops into the casserole, turn the funnel right side up and wash out all the fiber with a stream of Na_2SO_3 solution from the wash bottle. Wash the wire and plate and add the remaining Na_2SO_3. Bring the mixture to a boil, add 3 cc. of 10% NaOH and boil for 5 minutes. Again collect the fiber on the filter plate, wash with hot water until the washings are colorless, loosen up and expose to Cl as before.

With the wood of some broad-leaved species all of the lignin is removed by the first chlorination and, instead of coloring yellow the second time in Cl gas, the fiber bleaches to a pure white. With most coniferous woods the fiber turns yellow when exposed to Cl the second time. In that event continue the chlorination for 0.5 hour, wash the fiber and boil in alkaline Na_2SO_3 solution as before, and again expose to Cl gas. Except in very unusual cases the fiber will bleach when exposed to Cl the third time.

At whatever stage the fiber bleaches white, remove it immediately from the generator, wash on the filter plate with a large amount of water, transfer with the aid of water to a casserole, let stand under water for a short time, collect in a large-sized, tared Gooch crucible, and wash well with alcohol and finally with ether. Dry the product, at first at a gentle heat, and finally at 100–105° C. until the weight is constant or begins to increase.

Notes.—(1) It is almost impossible to wash out the last traces of acid, and unless the fiber is washed with alcohol and ether, the slow drying with the concentration of acid at the drying surfaces will cause a browning of the edge of the cellulose.

(2) If for any reason there should be any mineral matter present which would not be removed by the treatment, ignite the dried product and subtract the weight of the ash to obtain the pure cellulose.

Alpha, Beta, and Gamma Cellulose.—In certain individual uses of cellulose products, as for instance the manufacture of rayon (artificial silk) from wood-pulp, the suitability of the raw material is largely judged by the amount of alpha cellulose it contains. This is an empirical term used to designate that form of cellulose which is most resistant to the action of caustic alkali,

as distinguished from the less resistant forms designated as beta and gamma cellulose. The procedure for determining Alpha Cellulose in materials like wood-pulp is as follows:

Weigh out duplicate samples of 5 grams each of the air-dry pulp cut into small pieces, place in a 400-cc. beaker, and add 50 cc. of 17.5% NaOH solution at 20° C. Determine the strength of the NaOH solution by careful titration and adjust it so that it contains 17.5% (±0.1%) of actual NaOH, since Na_2CO_3 does not react.* Let stand a few minutes until the pulp has absorbed the caustic solution, disintegrate thoroughly with a flattened glass rod and add 50 cc. more of the NaOH solution. Let stand for ½ hour from the time the NaOH was first added, holding the temperature at 20° C. Add 300 cc. of water and filter through a washed linen filter cloth, using a 4-inch Büchner funnel and a large suction flask. (Save the filtrate.) Wash with 1 liter of water at 20° C., followed by 100 cc. of dil. acetic acid (1:4). Transfer the filtrate and washings to a 2-liter beaker and save for the determination of beta cellulose.

Wash the alpha cellulose on the filter cloth with 1 liter of boiling water, discarding these washings. Place the funnel containing the residue in the oven and when partly dry remove the linen filter and carefully scrape off the cellulose, transferring it to a weighing bottle. Dry in the weighing bottle at 105° C. for 2.5 hours, cool in a desiccator and weigh with the bottle tightly stoppered. Return to the oven and weigh at half-hour intervals until the cellulose gains in weight. From the lowest weight calculate the alpha cellulose in the air-dry pulp. Determine the moisture on a separate portion of the pulp by drying at 105° C. to constant weight and calculate the percentage of alpha cellulose on the bone-dry basis.

Determine Beta Cellulose in the filtrate from the alpha cellulose contained in the 2-liter beaker. Acidify the filtrate with acetic acid, digest on the water bath until the precipitate coagulates sufficiently to be collected by filtering under suction on a linen cloth filter. Wash with hot water until free from acid, transfer to a weighing bottle and dry until it begins to gain weight as described under Alpha Cellulose above. Calculate the weight of beta cellulose to percentage of the bone-dry sample.

* See p. 31.

Calculate Gamma Cellulose by subtracting the sum of the percentages of alpha and beta cellulose from the percentage of total cellulose, all on the bone-dry basis.

NOTE.—As the distinction between alpha, beta, and gamma cellulose is entirely empirical, the above directions must be followed exactly in order to obtain concordant results.

WOOD PULP SAMPLING AND TESTING

General.—The following procedures for sampling and testing wood pulp have been used in this laboratory for many years. The method for sampling machine-dried pulp in bales was originally developed in this laboratory and has been adopted as the official method of the American Pulp and Paper Association, the Association of American Wood Pulp Importers and the Technical Association of the Pulp and Paper Industry. A résumé of the requirements of the above Associations is given at the end of this method. At the present writing no method for sampling wood pulp in laps has been officially adopted for general use in this country, but the strip and wedge methods as here described are extensively used.

Wood pulp is produced and marketed under such a variety of conditions that it is impossible to have one method of sampling applicable to all forms. The strip method is well adapted for sampling at the pulp mill; the augur method is suitable for sampling baled pulp, but not for wet lap pulp. No method which involves the opening of the bales is suitable for sampling at the docks in transit, since the transportation companies will not handle broken bales. Accuracy in sampling depends more upon taking sufficient samples from individual units to secure a fair average of the lot than upon any particular method of cutting the samples.

SAMPLING

Machine-dried Pulp in Bales (Augur Method).—Sample only sound and intact bales. Weigh each bale before sampling and reject any abnormal bale. A bale is to be considered abnormal when it shows any indication of having been damaged or opened or when it differs from the standard mill weight by more than

10%. If the standard mill weight is 450 pounds, for example, reject any bales weighing more than 495 or less than 405 pounds.

Take the sample by boring into the bales to a depth of 3 inches with a special auger bit or with a machine cutter, using a single knife. (A sampler which has been found satisfactory is shown in Fig. 20.*) Remove the discs, which are approximately 4 inches in diameter, and take 10 of them as a sample, these to be selected as follows: One disc from the second sheet of the wrapper, 2 discs from a depth of 1 inch, 3 discs from a depth of 2 inches, and 4 discs from a depth of 3 inches. Sample at least 5% and preferably 10% of all the bales in a lot, but in no case sample less than 15 bales to represent 1 lot of pulp.

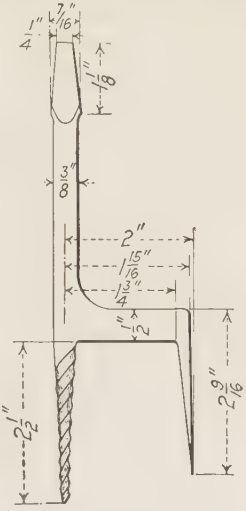


Fig. 20.—Pulp Sampling Knife.

Have the holes bored so located that in 5 successive bales they will represent a portion extending diagonally across the bale; the first hole to be bored at the corner, the edges of the cut being at a distance of 1 inch from the edge of the bale; the second cut half-way between the location of the first and the center; the third at the center, and so on until the fifth bale is sampled in the opposite corner in a position corresponding to the first.

Pulp in Rolls.—Sample at least 20% and preferably more of the rolls. Weigh the entire shipment if possible.

(*A*) Auger Method.—Take the sample by boring into the rolls in the same manner as for pulp in bales. Take the first sample so that the edge of the disc is within 1 inch of the end of the roll; the second half-way between the first and the center; the third at the center, and so on.

(*B*) Strip Method.—Cut a strip of definite width across the face of the roll from the second layer and 4 other similar strips from layers located at least 1.5 inches or farther from the outside layer. In the case of large lots a 1-inch strip is satisfactory; for small lots, however, the strips should be 3 inches wide.

* These may be obtained from the Millers Falls Co., Millers Falls, Mass.

Wet Pulp in Laps.—(*A*) STRIP METHOD.—(1) *Cutting of Sample.*—Take the sample by cutting a strip about 1 inch* wide from the center of the folded section to the middle of the outside edge, making the cut in each case half-way through the lap. Have the cuts made so located that in 4 successive laps they will represent a cross having its center at the center of the top face of the lap and each arm terminating in the center of one of the 4 edges (see Fig. 21). Sample the fifth lap in the same way as the first, and so on.

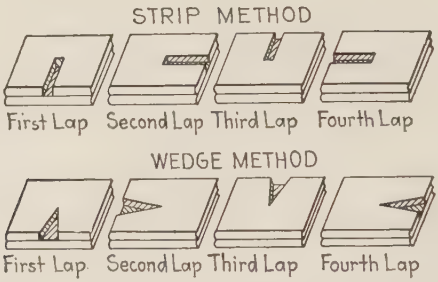


FIG. 21.—Methods of Sampling Pulp in Laps.

(2) *Selection of the Laps.*—When the pulp is loose in laps, sample not less than 1 lap in every 2000 pounds of wet pulp. In sampling from a car, take care that the sample laps fully represent every portion of the car With loose pulp it is necessary to weigh the whole carload or shipment.

When the laps are bundled together in bales, ascertain the total number of bales and weigh and sample not less than 2.5%† of this number. Open each bale to be sampled and withdraw 1 lap. Cut the samples from these laps as above described. Select the laps from the bales as follows:

From 20% of the bales sampled withdraw the middle lap.

From 40% of the bales sampled withdraw the lap halfway between the outside and the center.

From 35% of the bales sampled withdraw the lap next to the outside.

From 5% of the bales sampled withdraw the outside lap.

* A narrower or wider strip may be adopted, provided the same width is cut from every bale sampled.

† It is convenient to work with a multiple of 20.

In the case of those laps which are withdrawn from the outside of the bales, cut the sample on that side which formed the outer surface of the bale.

(*B*) Wedge Method.—The procedure in this method is similar to that in the strip method above, except that, instead of cutting strips a wedge is cut from each bale, the angle of the wedge being exactly 9 deg. and the wedge cut from the center of the lap to the edge. Make the depth of the cut half-way through the lap. The position of each cut is similar to that of the strip method, as shown in Fig. 21.

Note.—The wedge method theoretically is more accurate than the strip method as the wedges contain more nearly the correct proportion of wet edge than the strips. It has been our experience, however, that the strip method in the hands of the average sampler gives fully as reliable results. One objection to the wedge method is the tendency of breaking off the point of the wedge and consequent loss of some of the sample.

Machine Pulp at Mill.—In sampling pulp at pulp mills where it is coming from the wet machines, cut a strip 2 or 3 inches* wide across the entire width of the web, taking at least 1 such strip for every 2000 pounds of production. The total amount of pulp covered by the test should be weighed immediately after coming from the machines.

In the case of pulp coming from dryers in a continuous web, cut a similar strip representing at least every fifth bale or roll of production.

For wet pulp coming from the Rogers wet machine cut a 2- or 3-inch strip through the center of the sheet, alternating with and across the machine run. The sampling should be continuous through the lot and should give a total weight of sample of at least 1 kilogram for every 15 tons.

Testing of Samples

Place all samples immediately upon being taken in a suitable air-tight container, the cover of which must not be removed until after weighing. Then dry the samples in a suitable oven provided with good ventilation, at a temperature of 204–220° F. (95-105° C.) until successive weighings in a closed container, made after an interval of not less than 3 hours' drying, do not

* The strips must be the same width throughout the sampling.

show a variation greater than 0.1% of the original wet weight of the sample. Take the minimum weight as the final bone-dry weight. From the loss thus obtained calculate the total percentage of moisture. The difference between this and 100% will represent the percentage of bone-dry pulp. Air-dry pulp is understood to consist of 90% of absolutely dry pulp and 10% of water. The percentage of air-dry pulp is therefore calculated by dividing the bone-dry percentage by 0.90.

The scales used for weighing the samples must be accurate and sensitive to 1 gram or less. (If avoirdupois scales are used. they should be capable of weighing to 0.03 ounce or less.)

Official Method of American Pulp and Paper Association and Association of American Wood Pulp Importers

General.—All tests must be made by a chemist duly authorized and approved by the Joint Committee representing the Association of American Wood Pulp Importers and the American Pulp and Paper Association, and must be made strictly in accordance with the following instructions—otherwise the Committee reserves the right to withdraw the approval of any chemist at any time.

On retests in case of disputes not less than one-half of the parcel in question must be available for sampling.*

Chemists must have proper and adequate equipment for weighing and sampling the bales and for the weighing and drying of samples.

All sampling of pulp must be done by or supervised by the approved chemist personally, or by his competent *bona fide* assistants.

Each chemist must file with the Committee a complete list of his *bona fide* assistants, who will do the sampling, such list to have the approval of the Committee. The chemist will be held responsible for the correct sampling by his approved assistants.

* In case of dispute, a retest shall be made either by one chemist acting for and mutually agreed upon by both parties, or a "joint (re-)test" shall be made by chemists representing both parties. In the latter case only one set of samples shall be obtained from the bales weighed and these samples shall be dried in an oven approved by both chemists. Retests coming within 1% of the original air-dry weight of pulp as invoiced will be deemed to uphold the original invoice.

The Committee shall at any time have the privilege of investigating the sampling done by chemists or their assistants.

Every test certificate shall clearly state the name of the person who did the sampling.

The test certificates shall be uniform and in accordance with forms to be approved by the Committee, a sample draft of which will be furnished by the Committee to each chemist.

Number of Bales to be Sampled.—Except by previous agreement, not less than 10% of the entire shipment, and not less than 15 bales, shall be sampled; samples to be drawn only from sound and intact bales, from different sections of the entire shipment, and the analyst shall be careful to observe that no unusual conditions prevail in the selection of the bales. The accurate weight of all bales sampled is to be ascertained by a competent weigher before sampling. All bales weighed and no others are to be sampled, and whenever bales are numbered, the number is to be given in addition to the weight.

Method of Sampling.—The method of sampling is the same as previously described.

Weighing of Samples.—All samples must be either weighed by *accurate scales* immediately after being drawn from the bales or, where this is impracticable, must be put into air-tight metal cans; and due care must be used in the transportation of such samples until they can be properly weighed at the laboratory of the chemists. The entire bulk of samples selected from the bales must be dried out for the test. The temperature in the drying oven shall be as near to 212° F. as possible, but shall not exceed 220° F., nor be less than 204° F. Two successive weighings at least 2 hours apart should not show a variation of more than 0.1% of the wet weight and the minimum of these weights is to be taken as the final bone-dry.

SULFATE COOK LIQUOR

General.—In the usual sulfate process for making wood pulp the principal ingredients of the liquor used for cooking the wood are NaOH, Na_2SO_4, Na_2CO_3, and Na_2S. The active agents in the digestive process are NaOH and Na_2S, and it is stated that these combine with roughly 50% of the weight of the dried wood to form soluble organic sodium salts. The liquor used for cooking

wood is generally referred to as White Liquor, the residual liquor after the cooking as Black Liquor.

The waste sulfate liquor (Black Liquor), obtained from cooking pulp materials by the sulfate process, contains in addition to small amounts of silicate, various organic salts of sodium and also varying proportions of Na_2S, Na_2SO_4, Na_2SO_3, NaOH and Na_2CO_3

Black Liquor

Specific Gravity.—Determine the sp. gr. at 15.5° C. with the Westphal balance and calculate the gravity Baumé.

Total Solids.—Weigh out 100 grams of the material and dilute to 1 liter with water in a volumetric flask. Mix thoroughly and pipette into a weighed platinum dish 50 cc. (equivalent to 5 grams). Evaporate on the steam bath and then dry to constant weight at 105° C. There will be some loss of H_2S but the result will be approximately correct.

Ash.—Ignite the above residue until the carbon is burned off. In case it is not possible to burn off all the carbon, dissolve in water and filter through an ashless filter into a beaker. Ignite the filter paper in the same platinum dish. Cool and add the filtrate to the dish. Evaporate to dryness, ignite gently, cool in a desiccator and weigh.

Silica.—Moisten the ash above obtained with conc. HCl, warm, add a few cc. of water, evaporate to dryness on the steam bath, bake at least 1 hour at 120–140° C., take up with dil. HCl, heat to boiling, filter through a quantitative filter, wash with hot water, ignite strongly in a platinum dish and weigh as SiO_2. Save the filtrate.

Sodium Sulfate.—Pipette 25 cc. of the original sample into a beaker, add about 100 cc. of distilled water, make slightly acid with HCl and heat to boiling. Add 10 cc. of hot $BaCl_2$ solution slowly, drop by drop, boil for 0.5 hour, filter and wash with hot water. Ignite in a weighed platinum crucible. On account of the organic matter present, some of the $BaSO_4$ is likely to be reduced to BaS. Moisten the precipitate in the crucible with a few drops of dil. H_2SO_4. Again ignite, cool and weigh as $BaSO_4$. Calculate to Na_2SO_4 and also to Na_2O.

Calculation.—$BaSO_4 \times 0.6086 = Na_2SO_4$.

$BaSO_4 \times 0.2656 = Na_2O$.

Total Sodium.—To an aliquot of the original solution corresponding to 5 grams of the sample add an excess of HCl, evaporate to dryness and ignite to a *dull red heat.** All the sodium salts except the sulfate are decomposed to NaCl. The temperature must be kept low to avoid volatilization of the latter. Leach out the residue with hot water and filter. Cool and titrate the NaCl with 0.1 N $AgNO_3$ solution in the usual way, using Na_2CrO_4 as an indicator.

It is necessary to leach the residue thoroughly with small portions of hot water and to remove all the particles from the dish. For accurate work it is desirable to filter and ignite the residue on the filter gently in a platinum dish and again leach with water. The leaching should be continued until the filtrate gives no reaction with $AgNO_3$. Calculate the titration to Na_2O.

Calculation.—1 cc. 0.1 N $AgNO_3 = 0.003100$ gram Na_2O.

The sum of the Na_2O thus found and the Na_2O found present as sulfate gives the total sodium as Na_2O.

Sodium Sulfide (Volumetric Zinc Method).—Solutions.—(*a*) *Standard Zinc Solution.*—Dissolve 16.75 grams of pure, 30-mesh zinc in a small excess of HNO_3. Add sufficient NH_4OH to redissolve all the precipitate formed and then 50 cc. excess. Dilute to 2000 cc. (If any precipitate forms after dilution, insufficient NH_4OH was added.)

(*b*) *Ammoniacal Nickel Sulfate Indicator.*—Make an approximately 10% solution of nickel ammonium sulfate and add a slight excess of NH_4OH.

Titration.—From the solution previously prepared for Total Solids pipette out 100 cc. (equivalent to 10 grams of the original). Dilute to about 250 cc. in a beaker with distilled water and run in from a burette the standard zinc solution. The end-point is reached when a drop of the solution in the beaker added to 3 drops of the nickel sulfate indicator tested on a white spot plate no longer forms a black precipitate. From the number of cc. of zinc solution required calculate the amount of Na_2S.

Calculation.—1 cc. zinc solution = 0.0100 gram Na_2S.

Total Available Alkalinity.—Evaporate 25 cc. of the original sample to dryness in a platinum dish, ash over a Tirrill burner

* If SiO_2 has been determined, evaporate the filtrate there obtained to dryness, ignite gently, dissolve in water and titrate the NaCl.

(it is unnecessary to burn off all the carbon), and leach out the soluble salts with hot distilled water as in the determination of Total Sodium above. Cool the filtrate and titrate with 0.5 N acid and methyl orange. Calculate the titration to Na_2O and also to NaOH. This gives the alkalinity available for recovery.

CALCULATION.—1 cc. 0.5 N acid = 0.01550 gram Na_2O.
= 0.02000 gram NaOH.

Free Caustic Soda.—Pipette 100 cc. of the black liquor (calculate the weight from its sp. gr.) into a 500-cc. volumetric flask and add 50 cc. of 10% $BaCl_2$ solution. Shake and dilute to the mark with distilled water, freshly boiled and free from CO_2. Let settle clear. Pipette 50 cc. of the clear supernatant liquor (equal to 10 cc. of the original) into a beaker and titrate with 0.1 N HCl and phenolphthalein. Calculate to NaOH.

CALCULATION.—1 cc. 0.1 N acid = 0.004001 gram NaOH.

NOTES.—(1) The above determination must be corrected for Na_2S, if present, as the latter reacts to phenolphthalein when it is half neutralized, according to the reaction : $Na_2S + HCl = NaSH + NaCl$. Hence 1 cc. 0.1 N HCl = 0.007806 gram Na_2S. To apply the correction, therefore, calculate the weight of Na_2S which would be present in the amount of liquor taken for titration and divide by 0.007806. This will give the number of cc. of 0.1 N HCl required by the Na_2S. Subtract this from the total titration and calculate the difference to NaOH.

(2) If the liquid is too dark to obtain a satisfactory end-point, the phenolphthalein indicator solution may be used as an outside indicator on a white porcelain tile. Place 1 or 2 drops of phenolphthalein in each depression in the spot plate and during the titration mix 1 drop of the liquid with the indicator until the point is reached where no pink color develops within 2 minutes after mixing.

(3) According to Sutermeister,* the above method gives somewhat low results for free caustic on account of occlusion of the latter by the barium precipitate. He recommends adding 25 cc. of the black liquor to 400 cc. of water and 15 cc. of 40% $BaCl_2$ solution in a beaker and titrating directly with standard acid without filtering.

Sodium Carbonate.—Pipette 25 cc. of the original liquor into a white casserole and add 200 cc. of water. Titrate with 0.5 N HCl and methyl orange. This titration gives the alkalinity due to Na_2CO_3, NaOH, and Na_2S.† Subtract the equivalents

* "Chemistry of Pulp and Paper Making," 139 (1920).

† Also one-half of Na_2SO_3, if the latter is present.

of NaOH and Na_2S previously determined and calculate the difference to Na_2CO_3.

CALCULATION.—1 cc. 0.5 N HCl = 0.02650 gram Na_2CO_3.

Sodium Silicate.—The sodium silicate may be approximately calculated by multiplying the amount of SiO_2 by 1.258. This is for the formula $Na_2Si_4O_9$. In the presence of considerable amounts of sodium silicate the method of analysis is complicated and results by the above procedures are not strictly correct as regards NaOH and Na_2CO_3.

Total Alkalinity.—The total alkalinity of the liquor itself is obtained by direct titration with standard acid and methyl orange as described under the determination of Sodium Carbonate. Calculate the titration as Na_2O and also as NaOH.

CALCULATION.—1 cc. 0.5 N acid = 0.01550 gram Na_2O.
= 0.02000 gram NaOH.

WHITE LIQUOR

General.—The determinations of total solids, ash, total sodium and available alkalinity are not generally required on white liquor, but, if desired, may be made by the same procedures as described under Black Liquor.

Specific Gravity.—Determine as under Black Liquor.

Sodium Silicate and Silica.—Pipette 50 cc. into a platinum dish, add cautiously an excess of HCl, evaporate to dryness, and then bake for 1 hour or more at 120–140° C. Take up with HCl, dilute with water, filter, wash with hot water, ignite the residue in platinum with a blast lamp and weigh as SiO_2. An approximation of the sodium silicate ($Na_2Si_4O_9$) present may be obtained by multiplying the SiO_2 thus found by 1.258.

Sodium Sulfate.—Determine as under Black Liquor.

Sodium Sulfide.—Pipette 25 cc. of the liquor into a dry beaker of about 300-cc. capacity. Do not dilute with water. Run in from a burette an amount of ammoniacal $AgNO_3$ solution as close to the saturation point as can be estimated. (This can be done from a preliminary titration.) Then shake the contents of the beaker rather vigorously for 2 or 3 seconds. This causes the black Ag_2S to separate in thick lumps from the clear solution. Add another drop of the $AgNO_3$ solution from the burette. If this forms a heavy precipitate where the drop comes

in contact with the solution, add a few more drops, give the beaker a shake and repeat the additions until only a faint cloud appears in the clear solution. If the beaker is held over a white sheet of paper, the end-point may be easily determined within a single drop. The last drop necessary to complete the precipitation forms only a faint cloud in the clear solution. If then another drop is run in after shaking, instead of forming a faint dark cloud, it will remain as a clear colorless spot surrounded by the faintly distributed precipitate in the pale brownish solution.

NOTE.—If the silver solution is added in excess, it will all be distributed evenly through the solution and no amount of shaking will cause the Ag_2S to separate in lumps.

Ammoniacal Silver Nitrate Solution.—Dissolve 55.29 grams of pure metallic Ag in pure HNO_3, or dissolve 87.07 grams of pure $AgNO_3$ in water. Then add 250 cc. of conc. NH_4OH and dilute to 1 liter. (Keep protected from strong light and away from heat.) 1 cc. of this solution is equivalent to 0.02 gram of Na_2S.

Alkalinity.—(1) TOTAL ALKALI EXPRESSED IN TERMS OF Na_2O.—Pipette out 25 cc. of the liquor and titrate with 0.5 N acid and methyl orange. The number of cc. of acid used (call this *A*) represents the alkali existing in the solution as Na_2CO_3, NaOH, Na_2S, and one-half Na_2SO_3. Calculate it in terms of Na_2O.

CALCULATION.—1 cc. 0.5 N acid = 0.01550 gram Na_2O.

(2) SODA AS NaOH + Na_2S.—Pipette 25 cc. of the sample into a 100-cc. volumetric flask. Add 25 cc. of a 10% solution of $BaCl_2$ and make up to the mark with freshly boiled distilled water. Shake for a few minutes and let settle. Cool and draw off 50 cc. of the clear liquid and titrate with 0.5 N acid and methyl orange. The number of cc. multiplied by 2 indicates the amount of acid necessary to neutralize the NaOH and Na_2S in the sample. (Call this *B*.) The difference between *A* and *B* represents the number of cc. required to neutralize the Na_2CO_3 and $\frac{1}{2}$ the Na_2SO_3, barium sulfite being practically insoluble.

(3) SODA AS SULFIDE, SULFITE AND THIOSULFATE.—Make a rough titration of 10 cc. of the liquor with 0.1 N iodine, after acidifying with acetic acid. Then run out from a burette 0.5 cc.

less than the required amount of iodine into a beaker containing about 200 cc. of distilled oxygen-free water. Pipette into this 10 cc. of the liquor, make acid with acetic acid and complete the titration with 0.1 N iodine, using starch as indicator. This titration indicates the amount of Na_2S, $Na_2S_2O_3$ and Na_2SO_3 in the sample. (Call this titration *C*.)

CALCULATION.—1 cc. 0.1 N iodine = 0.003903 gram Na_2S.
= 0.003100 gram Na_2O.

(4) SODIUM THIOSULFATE AND SULFITE.—Pipette 50 cc. of the liquor into a 250-cc. volumetric flask. Add an excess of alkaline $ZnCl_2$ solution (made by adding NaOH to a $ZnCl_2$ solution in sufficient excess to redissolve the precipitate formed). Make up to the mark, shake for a few minutes and let settle. Draw off 100 cc. of the clear solution with a pipette and neutralize with 0.1 N H_2SO_4, using methyl orange. This converts the sulfites present into acid sulfites. When acid sulfites are titrated with iodine the following reaction takes place:

$$NaHSO_3 + H_2O + I_2 = NaHSO_4 + 2HI.$$

Hence 1 molecule of acid sulfite on titration with iodine liberates acid equivalent to 3 molecules of NaOH.

Titrate the neutralized solution with 0.1 N iodine solution and starch. (Call this *D*.) Then decolorize with 1 drop of 0.1 N thiosulfate solution and titrate till neutral with 0.1 N NaOH. The number of cc. of NaOH, multiplied by 0.0042, gives the amount of Na_2SO_3 in the aliquot; and this figure, divided by 0.0063, gives the number of cc. of 0.1 N iodine to which it is equivalent. Subtract this from the iodine titration previously obtained. Calculate the difference to $Na_2S_2O_3$.

CALCULATION.—1 cc. 0.1 N iodine = 0.01581 gram $Na_2S_2O_3$.

(5) FINAL CALCULATIONS.—$C - \frac{D}{2}$ gives the cc. of iodine equivalent to the Na_2S. (This is a check on the Na_2S by ammoniacal $AgNO_3$.)

$A - B$ gives the number of cc. required by the Na_2CO_3 and one-half the Na_2SO_3.

1 cc. 0.1 N iodine = 0.003903 gram Na_2S.
1 cc. 0.5 N acid = 0.02650 gram Na_2CO_3.
= 0.01550 gram Na_2O.

The titration *B*, expressed as Na_2O, minus the sodium sulfide titration (with ammoniacal $AgNO_3$), expressed as Na_2O, gives the Na_2O present as NaOH. Calculate this to NaOH by multiplying by 1.291.

NOTE.—The above methods under Alkalinity are those of Otto Kress, published in *Paper*, **17,** No. 24, 30 (1916).

REFERENCES.—The method for Sulfide in White Liquor is described by Carl Moe in *Paper*, **14,** No. 22, 19 (1914). See also article by Otto Kress in *Paper*, **17,** No. 24, 30 (1916); and articles by Carl Moe beginning in *Paper*, **18,** No. 12, 11 (1916), and by the same author in *Paper*, **13,** No. 24, 156 (1913).

BLACK ASH

General.—Black Ash is the ash recovered after evaporation and calcining of the liquor used in the soda and sulfate processes of pulp manufacturing. A typical analysis is given* as follows:

Sodium carbonate, Na_2CO_3	78.15%
Caustic soda, NaOH	1.83
Sodium sulfate, Na_2SO_4	2.55
Sodium sulfide, Na_2S	0.50
Salt, NaCl	6.60
Carbon, C	4.30
Silica, SiO_2	5.10
Calcium carbonate, $CaCO_3$	0.72
Undetermined	0.25

The following determinations are usually sufficient:

Carbon and Insoluble Matter.—To 40 grams of the finely ground sample in a large beaker add about 500 cc. of water and boil gently for about 1 hour. Filter through a filter paper, previously dried and weighed in a weighing bottle, collecting the filtrate in a liter volumetric flask; wash thoroughly with hot water, dry at 100° C. and weigh in the same weighing bottle as Carbon and Insoluble Matter. Then ignite in a platinum crucible until the carbon is completely burned off. Cool in a desiccator and weigh the insoluble matter. Report the loss in weight as Carbon.

Caustic Soda.—Cool the filtrate from the above determination to room temperature, dilute to 1 liter and mix thoroughly. Call this solution *A*. Pipette 50 cc. of the solution (equivalent to 2

* "Standard Methods for Testing Materials in the Pulp and Paper Industry," *Tech. Assoc. P.P.I.* (1924).

grams) into a 250-cc. volumetric flask and precipitate carbonates with a slight excess of neutral $BaCl_2$ solution. Dilute to the mark with freshly boiled and cooled water. Shake thoroughly, let settle, pipette out 100 cc. of the clear liquid (equivalent to 0.8 gram of the original sample) and titrate with 0.1 N HCl and methyl orange. From this titration subtract 0.49 cc. for each percentage of Na_2S (as determined below). Calculate the difference to NaOH.

CALCULATION.—1 cc. 0.1 N HCl = 0.004 gram NaOH.

Sodium Sulfide.—To 80 cc. of recently boiled water in a flask add 25 cc. of solution *A* (equivalent to 1 gram of the sample). Acidify with acetic acid and titrate at once with 0.1 N Iodine, using starch as an indicator. Calculate the titration to Na_2S.

CALCULATION.—1 cc. 0.1 N iodine = 0.0039 gram Na_2S.

Sodium Carbonate.—Pipette 25 cc. of solution *A* into a flask. Dilute to about 100 cc. with water and titrate with 0.5 N HCl and methyl orange. Subtract from the titration the amount of 0.5 N HCl equivalent to the NaOH and the Na_2S (*i.e.*, $\frac{1}{4}$ of the number of cc. of 0.1 N HCl required by the titration under Caustic Soda) and calculate the difference to Na_2CO_3.

CALCULATION.—1 cc. 0.5 N HCl = 0.0265 gram Na_2CO_3.

Salt.—Pipette 25 cc. of solution *A* into a small flask, make slightly acid with dil. HNO_3 and boil to expel H_2S. Filter and wash the residue. Cool the filtrate, add an excess of powdered $CaCO_3$ and about 1 cc. of chromate indicator solution, and titrate with 0.1 N $AgNO_3$ solution until a reddish color appears and remains after stirring. Calculate to NaCl.

CALCULATION.—1 cc. 0.1 N $AgNO_3$ = 0.005845 gram NaCl.

Sodium Sulfate.—To 500 cc. of solution *A* add an excess of HCl, boil to expel CO_2, and precipitate while boiling with a slight excess of $BaCl_2$, added drop by drop. Boil for 5 minutes, let stand overnight protected from SO_3 fumes, filter, wash thoroughly with hot water, dry, ignite in a weighed platinum crucible, cool in a desiccator, and weigh as $BaSO_4$. Calculate to Na_2SO_4.

CALCULATION.—$BaSO_4 \times 0.6086 = Na_2SO_4$.

SULFITE ACID

General.—Sulfite Acid or Bisulfite Liquor is the liquid used for cooking wood to make pulp by the well-known sulfite

process. It consists of an aqueous solution of calcium and magnesium bisulfites with an excess of sulfurous acid. As the SO_2 gas from which it is made always contains a little SO_3, the finished acid liquor will contain more or less $CaSO_4$ as an impurity.

Specific Gravity.—Determine with the Westphal balance or a pycnometer, preferably the former.

Total Sulfurous Acid.—Measure out 10 cc. of the acid and make up to 100 cc. in a volumetric flask. Pipette 10 cc. of the diluted acid into an excess of 0.1 N iodine and titrate with 0.1 N thio, using starch solution as an indicator. Calculate the iodine consumed to SO_2.

CALCULATION.—1 cc. 0.1 N iodine = 0.0032 gram SO_2.

Free Sulfurous Acid.—Titrate 25 cc. of the diluted solution with 0.5 N NaOH, using phenolphthalein as an indicator. Calculate to SO_2.

CALCULATION.—1 cc. 0.5 N NaOH = 0.016 gram SO_2.

Sulfur Trioxide.—Measure out 25 cc. of the original solution, add 5 cc. of conc. HCl, and boil until the SO_2 is completely expelled. To the boiling solution add 10% $BaCl_2$ solution, drop by drop, in excess. Boil for 30 minutes, let stand till clear, filter, ignite and weigh as $BaSO_4$. Calculate to SO_3.

CALCULATION.—$BaSO_4 \times 0.3430 = SO_3$.

Lime and Magnesia.—Pipette out 25 cc. of the original solution, add about 1 cc. of conc. H_2SO_4, evaporate to dryness in a platinum dish, ignite carefully, cool and weigh the mixed sulfates as $CaSO_4 + MgSO_4$.

Dissolve the residue in 25 cc. of dil. HCl, wash the solution into a beaker, make alkaline with NH_4OH, heat to boiling and add enough $(NH_4)_2C_2O_4$ solution to precipitate completely the lime. Continue the boiling for 2 minutes, and let the precipitated CaC_2O_4 settle for $\frac{1}{2}$ hour. Filter, wash with hot water, ignite in a platinum crucible over a blast lamp to constant weight and weigh as CaO. Calculate the CaO to $CaSO_4$, deduct from the mixed sulfates and calculate the $MgSO_4$ to MgO.

CALCULATION.—$CaO \times 2.4279 = CaSO_4$.

$MgSO_4 \times 0.3349 = MgO$.

NOTE.—The Ca and Mg sulfates may also be separated as follows: Add 10 cc. of water and 1 or 2 drops of HCl, which will dissolve all the $MgSO_4$. Add 1 or 2 drops of conc. H_2SO_4 and 25 cc. of 95% alcohol. Let stand for 1

hour, filter and wash with 60% alcohol to remove acid. Finally wash with 40% alcohol as long as anything is dissolved. Ignite and weigh the residue as $CaSO_4$.

Results.—The results should be expressed as follows:

Sulfurous Acid (SO_2)
Sulfuric Acid (SO_3)
Lime (CaO)
Magnesia (MgO)

Equivalent to:

Calcium Sulfate ($CaSO_4$)
Calcium Bisulfite (CaS_2O_5)
Magnesium Bisulfite (MgS_2O_5)
Free Sulfurous Acid (SO_2)

The SO_3 is calculated to $CaSO_4$. The remaining CaO is calculated to CaS_2O_5 and the MgO is calculated to MgS_2O_5. The excess SO_2 is expressed as Free SO_2.

The so-called "*Mill Test*" is expressed as follows:

"Free" Sulfurous Acid.
"Combined" Sulfurous Acid.
Total Sulfurous Acid.

The "free" sulfurous acid is the actual free SO_2 plus one-half of the SO_2 in the CaS_2O_5 plus one-half of the SO_2 in the MgS_2O_5, and should check approximately with the figure obtained by the titration with KOH. It is, more strictly speaking, the "available SO_2." The "combined" sulfurous acid is the sum of one-half of the SO_2 in the CaS_2O_5 and one-half of the SO_2 in the MgS_2O_5.

NOTES.—(1) The "free" and "combined" SO_2 together should be the same as the total SO_2 determined by titration with iodine.

(2) Griffin and Little* give the following as a typical analysis of a well-made liquor prepared from dolomite:

Sp. gr. at 15° C	1.0582
Total SO_2	4.41%
SO_3	0.13%
CaO	0.95%
MgO	0.72%
Combined as:	
$CaSO_4$	0.22%
CaS_2O_5	2.84%
MgS_2O_5	3.04%
Free SO_2	0.11%

* "The Chemistry of Paper Making," 228.

This would give a "Mill Test" as follows:

Free SO_2	2.26%
Combined SO_2	2.15%
Total SO_2	4.41%

The tendency today is toward a high "free SO_2," 2.50–3.20%, and a lower combined SO_2, 1.20–1.35%. For cooking dry wood a suitable ratio is (approximately):

Total SO_2: "free" SO_2: "combined" $SO_2 = 4:3:1$.

For wet wood the "combined" SO_2 should be higher.

Factors.—The following factors will be found useful in calculating the final combinations:

$SO_3 \times 1.700 = CaSO_4$.
$CaO \times 3.285 = CaS_2O_5$.
$MgO \times 4.178 = MgS_2O_5$.
$CaS_2O_5 \times 0.6956 = SO_2$.
$MgS_2O_5 \times 0.7606 = SO_2$.

ALUM

General.—This method is for the "alum" used by papermakers, which is not a true alum but a basic sulfate of alumina, approximately $Al_2(SO_4)_3 \cdot 14H_2O$.

Insoluble Matter.—Dissolve 25 grams of the sample in about 200 cc. of boiling water and filter rapidly through a weighed Gooch crucible with suction. Wash the residue on the filter with hot water, dry at 105° C. and weigh.

Solution No. 1.—Collect the filtrate and washings in a 500-cc. volumetric flask, cool, dilute to 500 cc. and thoroughly mix.

Solution No. 2.—Transfer 100 cc. of Solution No. 1, equivalent to 5 grams of alum, to another 500-cc. flask, make up to the mark with distilled water, and thoroughly mix.

Alumina.—Pipette out 50 cc. of Solution No. 2, equivalent to 0.5 gram of alum, and acidify with 10 cc. of conc. HCl and 4–5 drops of conc. HNO_3. Heat to boiling. Add 10 cc. of 10% NH_4Cl solution and a pinch of tannic acid on the end of a spatula, and then NH_4OH until barely alkaline. Boil until there is only a faint smell of NH_3. Add about one-fourth of a 9-cm. filter paper which has been boiled with a little water until the fibers are thoroughly disintegrated. (This aids in igniting the precipi-

tate by keeping it from drying into a hard, horny mass.) Let the precipitate settle, filter and wash free from chlorides. Dry the precipitate in the oven in a weighed platinum crucible, then ignite over a blast lamp to constant weight, and weigh as $Fe_2O_3 + Al_2O_3$. To obtain the amount of alumina, determine the Fe_2O_3 separately as below and deduct from this weight.

Sulfur Trioxide.—Acidify 100 cc. of Solution No. 2 with HCl and heat to boiling. Then add 10% $BaCl_2$ solution slowly, drop by drop, as long as it produces a precipitate. Boil one-half hour. (Or, boil 5 minutes and let stand overnight.) Let the precipitate settle completely, filter, wash, ignite and weigh as $BaSO_4$. (Test the filtrate with more $BaCl_2$ to insure complete precipitation.) Calculate to SO_3.

CALCULATION.—$BaSO_4 \times 0.3430 = SO_3$.

Iron.—Transfer 100 cc. of Solution No. 1 to a 200-cc. beaker and add 5 cc. of conc. H_2SO_4 and 0.1 N $KMnO_4$, drop by drop, till a permanent pink forms. Pass this solution through the Jones reductor (see p. 186) and titrate to a faint pink with 0.1 N $KMnO_4$ solution.* Calculate the iron as Fe_2O_3.

CALCULATION.—1 cc. 0.1 N $KMnO_4 = 0.008$ gram Fe_2O_3.

NOTE.—In case it is impossible to get the reductor so that a single drop of the $KMnO_4$ will color the washing solution, run a blank on the reductor, using the same amounts of reagents and washings, and subtract the blank titration from the titration required by the sample.

Zinc.—Add $(NH_4)_2S$ in excess to the filtrate from the Al_2O_3 precipitate and let stand some time. Filter, wash with H_2S water, and dissolve the ZnS precipitate in dil. HCl. Make alkaline with NH_4OH, add 1 drop of litmus solution and HNO_3 until the litmus just turns red. Heat nearly to boiling and add slowly ammonium phosphate solution containing a weight of phosphate equal to about 12 times that of the Zn to be precipitated. Keep the solution just below boiling point for about 15 minutes, or until the precipitate has become crystalline. Let the solution cool for at least 4 hours and then filter on a Gooch crucible. Wash with a 1% solution of ammonium phosphate until free from sul-

* For alums containing a very small amount of Fe use 0.01 N $KMnO_4$ for titrating both the sample and the blank. If extreme accuracy is desired a larger sample may be used.

tate, then wash 5 times with alcohol. Dry at 105° C. to constant weight and weigh as $ZnNH_4PO_4$. (It may also be ignited and weighed as $Zn_2P_2O_7$.)

Complete precipitation of the Zn depends on the neutrality of the solution and it is absolutely necessary to test the filtrate for Zn by adding NH_4OH and a few drops of $(NH_4)_2S$ and allowing it to stand for some time.

CALCULATION.—$ZnNH_4PO_4 \times 0.3664 = Zn.$

$Zn_2P_2O_7 \times 0.4290 = Zn.$

Lime.—Boil the filtrate from the Zn precipitate to expel H_2S, make alkaline with NH_4OH and add $(NH_4)_2C_2O_4$ solution in excess. Filter, wash, ignite in the blast and weigh as CaO.

Basicity or Acidity.—The following method* is based on the fact that an excess of neutral KF decomposes aluminum salts, forming two stable compounds reacting neutral to phenolphthalein, while any free acid remains unaltered, thus:

$$Al_2(SO_4)_3 + (H_2SO_4) + 12KF = 2(AlF_3 \cdot 3KF) + 3K_2SO_4 + (H_2SO_4).$$

SOLUTIONS REQUIRED.—(1) *0.1% alcoholic solution of phenolphthalein.*

(2) *KF solution*, prepared by dissolving 1000 grams of pure KF in 1200 cc. of hot CO_2-free distilled water, adding 5 cc. of phenolphthalein solution and neutralizing if necessary with KOH or H_2SO_4 (or HF) until about 1 cc. in 10 cc. of distilled water shows a faint pink color. Filter out any insoluble matter without washing and dilute the clear filtrate to 2000 cc. with CO_2-free water. Preserve in a wax bottle or a glass bottle coated inside with wax.

(3) *Standard 0.5 N H_2SO_4* and *0.5 N KOH*, free from Al_2O_3 and similar bases. Standardize the alkali against the acid in about 80 cc. of distilled water to which 2 cc. of the above KF solution have been added, using phenolphthalein indicator.

PROCEDURE.—Place exactly 68 cc. of Solution No. 1, equivalent to 3.40 grams of the sample, in a 4-inch casserole. Add about 35 cc. of distilled water and heat to boiling. To the solution add exactly 10 cc. of 0.5 N H_2SO_4. Cool to room temperature; add 20 cc. of KF solution and 0.5 cc. of phenol-

* *J. Soc. Chem. Ind.*, **30**, 134 (1911).

phthalein solution. Titrate with 0.5 N KOH (do not use NaOH), adding it drop by drop until a slight pink persisting for 1 minute is obtained. The titration shows whether the material is basic or acid as follows:

Basic Al_2O_3.—When the KOH back titration is less than the amount of H_2SO_4 added, then

Percentage of free Al_2O_3 = (cc. of H_2SO_4—cc. of KOH) $\times 0.25$.

Free H_2SO_4.—When the KOH back titration is greater than the amount of H_2SO_4 added, then

Percentage of free H_2SO_4 = (cc. of KOH—cc. of H_2SO_4) $\times 0.72$.

Neutrality.—If the back titration is equal to the H_2SO_4 added, then the alum is neutral.

NOTE.—Darkening of the solution during the back titration with KOH indicates an insufficient amount of KF added. In such cases repeat the test with a fresh solution and a larger amount of KF. Ammonium salts, if present, must be expelled by boiling the sample with an excess of standard KOH and this excess determined. Also if much iron salts are present, an increased quantity of KF solution may be required.

Calculation of Results.—It is seldom that papermakers' alum contains Zn or more than traces of lime, titanium, etc. Under ordinary circumstances the results should be reported as follows:

Insoluble Matter
Alumina (Al_2O_3) (soluble in water)
Sulfur Trioxide (SO_3)
Iron, calculated as Ferric Oxide (Fe_2O_3)

Equivalent to:

Insoluble Matter
Ferrous Sulfate ($FeSO_4$)
Aluminum Sulfate [$Al_2(SO_4)_3$]
Basic Alumina (Al_2O_3)*
Water (by difference).

The Fe_2O_3 is all calculated to $FeSO_4$, although as a matter of fact more or less of it is generally present in the oxidized state. The remaining SO_3 is calculated to $Al_2(SO_4)_3$. Any Al_2O_3 left over is reported as basic Al_2O_3. In case the sample contains free acid, the Fe_2O_3 is calculated to $FeSO_4$ as above, the total Al_2O_3 to $Al_2(SO_4)_3$, and the remaining SO_3 to free H_2SO_4.

* Or, Free Sulfuric Acid (H_2SO_4).

Factors.—The following factors will be found useful:

$Fe_2O_3 \times 1.9026 = FeSO_4$.
$Al_2O_3 \times 3.3562 = Al_2(SO_4)_3$.
$Al_2(SO_4)_3 \times 0.2980 = Al_2O_3$.
$Al_2(SO_4)_3 \times 0.7020 = SO_3$.
$Fe_2O_3 \times 1.0028 = SO_3$ in equiv. am't of $FeSO_4$.
$SO_3 \times 1.2250 = H_2SO_4$.
$SO_3 \times 1.4244 = Al_2(SO_4)_3$.

DYES AND PIGMENT COLORS

General.—This method is for the testing of aniline dyes and pigment colors for use in coloring paper. (See also p. 444.)

Strength and Brilliancy.—Stock.—As colors behave differently on different fibers, it is advisable when possible to make the tests with the stock on which the color is to be used. When this is not known, and for routine tests, use bleached sulfite made up into stock in the proportions of 1 gram of bone-dry fiber to about 300 cc. of water. This is preferably prepared in a small beater as follows: Furnish 250 grams of sulfite pulp and the required amount of water; brush out for 1 hour; then raise the roll and brush again for ½ hour to remove knots. Keep the stock in a large, covered jar and make a moisture determination each day it is used.

Color Solution.—In the case of dyes dissolve 0.5 gram in about 100 cc. of hot (but not boiling) water and dilute to 500 cc. in a volumetric flask. For pigments make up 5 grams to 500 cc. with hot or cold water.

Mordants.—Dilute solutions of salt, lead acetate, and soda ash are required as mordants for certain colors.

Procedure.—Weigh out into a 2000-cc. beaker or enamel pot an amount of the stock equivalent to 5 grams bone-dry and add sufficient water to make the volume about 250 cc. Then add 5 cc. of a 2% rosin size solution, stir for 5 minutes, add 5 cc. of a 4% alum* solution, stir for 5 minutes longer and add 10 cc. of the color solution. (In testing direct-color dyes, add the dye solution first, stir for 5 minutes, add the rosin size, stir 5 minutes and

* Papermaker's alum, $Al_2(SO_4)_3 \cdot 18H_2O$.

finally add the alum and heat the mixture to 120° F.). This will give a sheet containing, on the weight of the bone-dry fiber, 2% of size, 4% of alum and 0.2% of dye (or 2% of pigment color).

In testing pigments add 0.5 gram of china clay mixed with 50 cc. of water just before adding the pigment. This produces a more uniform coloring of the sheet. Mix the stock well by stirring for at least ½ hour (1 hour for chrome and earth pigments) with a mechanical stirrer or egg beater, or by transferring to a quart Mason jar and shaking violently for 5-10 minutes. Finally add about 1200 cc. of water, mix and make a hand sheet on a suction mold. After forming the sheet, couch it on a strip of absorbent paper, fold the absorbent paper over the sheet and mark it with the strength of the dye. Squeeze out the surplus moisture by passing through a wringer. Remove the dyed sheet, punch a hole near the edge, and suspend it on a copper wire or glass rod in the drying oven at a temperature of about 85° C.

Make up a series of sheets from the standard color with which the sample is to be compared, following exactly the same procedure except to vary the percentage of dye. For preliminary comparison use 0.15, 0.20 and 0.25% of the standard dye (or ten times these amounts of standard pigment).

After the sheets are dry, compare them for color-strength and brilliancy, getting the light from different angles and comparing both sides of the sheets. After deciding which of the standard sheets most nearly matches the sample, make up another set of standards within the range of the one which most nearly matches and varying from each other by 0.005% of dye. After having obtained a match, calculate the percentage strength of the sample as compared with the standard by dividing the strength of the standard sheet which the sample matches by 0.2 and multiplying by 100.

Example.—On preliminary test the sample falls between the standard sheets containing 0.20 and 0.25% of dye. Make up a new series of standards containing 0.205, 0.210, 0.215%, etc. The sample is found to match the 0.225% sheet. Then the strength of the sample is $\frac{0.225}{0.2} \times 100 = 112.5$ %.

Notes.—(1) A convenient method of permanently marking sample sheets is to use an indelible pencil after passing the sheets through the wringer.

(2) In testing the yellow dyes, it is a help to add methylene blue or safranine, using a constant quantity of about 25% of the amount of yellow used. Samples so made are compared for shade rather than strength.

Alternative Method for Pigment Colors.—Weigh an amount of the stock fiber equivalent to 10 grams bone-dry into a porcelain mortar. Add exactly 0.5 gram of the pigment. (In the case of carbon black use only 0.05 gram). Mix the contents of the mortar thoroughly with a pestle, adding a little water if necessary but keeping the amount at a minimum which will allow easy mixing. Stir with the pestle for about 10–15 minutes, or until a uniform color is obtained. Transfer to a large bottle, dilute to 1 liter with water, add 10 cc. of 2% rosin size solution, shake thoroughly, add 10 cc. of 4% alum solution and shake again. Form a sheet from this mixture and compare with standards as above.

Fastness.—Expose a portion of the dyed sheet to the ultra-violet light or the Fade-ometer and examine for fading at frequent intervals. A color which shows marked fading within $1\frac{3}{4}$ hours ultra-violet light or 10 hours Fade-ometer exposure is not generally considered sufficiently fast for ordinary use; whereas one which shows very little fading after 5 hours exposure to ultra-violet or 30 hours to the Fade-ometer is considered a relatively fast color.

BLANC FIXE

General.—Blanc Fixe is generally marketed as a paste of $BaSO_4$ and water, less commonly in the dry form. The commercial blanc fixe often also contains more or less phosphate and impurities such as carbonates, sulfites, organic matter, silica, heavy metals and alkali metals. It is quite often the case that a blanc fixe is practically pure as it leaves the factory but takes up impurities on standing in the storage barrels. It is claimed that it is bad to store it in oak barrels, as a yellow stain nearly always develops. It should preferably be stored in fir barrels.

Blanc fixe in the pulp form (paste) should not contain more than 30% of moisture, and both pulp and dry forms should contain not less than 97.5% of $BaSO_4$ on the dry basis.

As a general rule the determinations of water, organic and volatile matter, and total $BaSO_4$ are sufficient, but it is sometimes

desirable to determine the amount and nature of the impurities and accordingly the following complete scheme is given:

Qualitative Tests.—As the source of raw materials and methods of manufacture determine the presence of certain impurities, a qualitative analysis should be made before proceeding with the quantitative determination.

Where the blanc fixe is intended solely for *photographic* purposes, test the sample first with $AgNO_3$ as follows: Spread a small sample on a glass plate with a spatula and apply a drop of 10% $AgNO_3$ solution. If a deep brown or blackish stain develops within 5 minutes *in the dark*, the sample is unfit for photographic purposes. Failure to meet this test, however, does not disqualify it as a filler or for coating ordinary paper.

Organic Matter.—A rough qualitative test for organic matter is to heat about 1 gram in a test-tube with 5–10 cc. of conc. H_2SO_4 and let settle. If organic matter is present the acid will turn brown.

Silica.—If a half-gram sample dissolves completely in 5–10 cc. of hot conc. H_2SO_4, the absence of SiO_2 is indicated.

Lead.—Boil 5 grams with saturated ammonium acetate solution and filter. To the filtrate add a solution of $K_2Cr_2O_7$. A yellow precipitate indicates Pb.

Iron and Alumina.—Heat 5 grams with 25 cc. of dil. HNO_3 (1 : 1) and filter. Add a slight excess of NH_4OH to the filtrate and heat. A flocculent precipitate indicates alumina, if white, and iron and alumina, if brownish.

Alkalies.—Tests for the alkalies and ammonia are made on the water solution in the usual way.

Moisture.—Weigh out rapidly 5 grams of the sample and dry to constant weight at 100° C. Report the loss as Moisture.

Loss on Ignition.—Ignite strongly the residue from the moisture determination, cool in a desiccator and weigh. Repeat until constant weight is obtained. The loss indicates organic and volatile matter. Previous qualitative tests will indicate whether a part of this loss is due to carbonate.

Water-soluble Material.—Digest 5 grams of the sample in 150 cc. of hot water. Filter and wash with hot water. Evaporate the filtrate to dryness in a weighed platinum dish and dry to constant weight at 100° C.

Acid-soluble Material.—Transfer the residue on the filter paper from the water-soluble determination to the beaker containing the remaining residue, and treat the whole with 125 cc. of hot dil. HCl (1 : 3). Filter and wash. Evaporate the filtrate and washings to dryness in a weighed platinum dish and dry at 100° C. to constant weight.

Iron Oxide and Alumina.—If the acid-soluble material is high, the presence of Fe_2O_3, Al_2O_3 $BaCO_3$ or $Ba_3(PO_4)_2$ is indicated. If phosphate is absent, take up the acid soluble residue with a little HCl and 100 cc. of water. Make the solution slightly alkaline with NH_4OH; boil, filter, wash with hot water, and ignite the precipitate, finally with a blast lamp; cool in a desiccator, and weigh as $Al_2O_3+Fe_2O_3$. If phosphate is present, add to the acid solution a known amount of Fe_2O_3 in the form of chloride or sulfate (see p. 37), then make slightly alkaline with NH_4OH and proceed as above. Subtract the known amount of Fe_2O_3 added. The resulting figure will be $Fe_2O_3+Al_2O_3+P_2O_5$ in the sample. Determine the P_2O_5 on a separate portion by the molybdate method as described below under Barium Phosphate, and subtract to get $Fe_2O_3+Al_2O_3$.

Barium Carbonate (and Phosphate).—To the filtrate from the above add a slight excess of HCl, heat to boiling, and then add slowly an excess of dil. H_2SO_4. Boil until the precipitate settles clear; filter, ignite, cool in a desiccator and weigh as $BaSO_4$. Calcultate to $BaCO_3$ or $Ba_3(PO_4)_2$ according to the qualitative analysis.

Calculations.—$BaSO_4 \times 0.8456 = BaCO_3$.

$BaSO_4 \times 0.8599 = Ba_3(PO_4)_2$.

Lime and Magnesia.—These are not often present in commercial blanc fixe but may be determined in the filtrate from the Barium Carbonate determination above in the usual way.

Lead Sulfate.—If the qualitative tests showed Pb, boil with saturated ammonium acetate solution the sulfate residue from the acid-soluble treatment. Filter and wash. Add a few drops of acetic acid and then a slight excess of bichromate solution. Heat to boiling, filter through a weighed Gooch crucible, wash with hot water, dry at about 100° C., set the Gooch crucible in a larger platinum crucible, ignite gently and weigh as $PbCrO_4$. Calculate to $PbSO_4$.

CALCULATION.—$PbCrO_4 \times 0.9383 = PbSO_4$.

Barium Sulfate.—Dry the residue from the ammonium acetate treatment (or, if Pb is absent, the residue from the acid-soluble treatment) to constant weight and calculate its percentage of the original sample. Then weigh out 1 gram of this dry residue, mix with 5–7 grams of pure Na_2CO_3 and fuse in a platinum crucible to a thin liquid. Digest the fusion with hot water until completely disintegrated; filter and wash *thoroughly* with hot water. Make the filtrate slightly acid with dil. HCl, dilute to 350 cc. and heat to boiling. Then add 25 cc. of 10% $BaCl_2$ solution, drop by drop from a pipette. Boil for 5 minutes, let stand overnight, filter, wash with hot water, ignite and weigh as $BaSO_4$. Calculate to the original basis.

NOTE.—In case the complete analysis is not desired, determine $BaSO_4$ as above, using 1 gram of the dry material from the moisture determination; then wash the residue from the fusion with hot water into a beaker and treat the filter paper with warm dil. HCl, collecting this in the same beaker. The whole precipitate should dissolve completely in HCl. Dilute this solution to about 350 cc., boil gently to expel the CO_2 and add a slight excess of dil. H_2SO_4, drop by drop. Let stand overnight. Filter out the $BaSO_4$, ignite and weigh as usual.

These two determinations give the total SO_3 as $BaSO_4$ and the total Ba as $BaSO_4$; and in a pure blanc fixe they should check closely. An excess of total Ba indicates soluble Ba salts [in the absence of $Ba_3(PO_4)_2$] and an excess of total SO_3 indicates other sulfates.

Barium Phosphate.—Boil 2 grams of the original material with 150 cc. of water, filter and wash by decantation; return the residue to the original beaker and boil with 100 cc. of water and 5 cc. of conc. HNO_3. Filter and wash with hot water. To the warm filtrate add an excess of ammonium molybdate solution. Let stand until the precipitate settles clear, then filter and wash with a 2% HNO_3 solution. Dissolve the yellow precipitate from the filter paper with dil. NH_4OH. The total volume should be between 50 and 100 cc. Add 25 cc. of magnesia mixture, stir well and let stand 1 hour. Filter on a weighed Gooch crucible and wash with 5% NH_4OH. Ignite strongly and weigh as $Mg_2P_2O_7$. Calculate to P_2O_5 and to $Ba_3(PO_4)_2$.

CALCULATIONS.—$Mg_2P_2O_7 \times 0.6379 = P_2O_5$.

$P_2O_5 \times 4.239 = Ba_3(PO_4)_2$.

$Mg_2P_2O_7 \times 2.704 = Ba_3(PO_4)_2$.

General Calculations.—If the material contains carbonates and phosphates, the acid-soluble Ba may be present in both forms and the amounts can be calculated from the total acid-soluble Ba and from the P_2O_5, figuring the latter to $Ba_3(PO_4)_2$ as above described and then the excess of Ba to $BaCO_3$.

If neither phosphate nor carbonate is present, the soluble Ba is probably in the form of chloride or sulfide. The Pb should be calculated to $PbSO_4$. The Fe and Al may be present as sulfates but are generally reported as oxides.

CALCULATIONS.—$Ba_3(PO_4)_2 \times 1.1630 = BaSO_4$.

$BaSO_4 \times 0.8456 = BaCO_3$.

REFERENCE.—This method is based on that described by A. B. Hutchins of the Ansco Co., Research Laboratory, published in *Paper* **20,** No. 13, 11 (1917), somewhat modified by experience in this laboratory.

BLEACH

(BLEACHING POWDER AND BLEACH LIQUOR)

General.—Bleaching powder, often called in the trade Bleach or Chloride of Lime, is made by passing chlorine over slaked lime at a temperature of 40–55° C. At higher temperatures than this a considerable amount of chlorate may be formed. Chemically, bleaching powder is probably calcium chloro-hypochlorite, $CaOCl_2$. When treated with water it forms chloride and hypochlorite according to the reaction: $2CaOCl_2 = CaCl_2 + CaO_2Cl_2$. The chlorine from the hypochlorite is the bleaching agent and ordinarily the only determination required is that of Available Chlorine.

Available Chlorine.—Mix the whole sample quickly and thoroughly, discarding the outside (top layer) which has lost more or less chlorine. Weigh out from a weighing bottle* about 10 grams into a porcelain mortar, add a little water and rub the mixture to a smooth cream. Then stir in more water with the pestle, let settle for a few moments and pour off through a funnel into a liter volumetric flask. Again rub up the sediment with water and pour off as before. Repeat the operation until the whole of the material has been conveyed into the flask without loss and the mortar washed clean. Then fill the flask to the mark with water, mix well and pipette out immediately, without allow-

* Keep the bottle covered while in the balance case as Cl is very corrosive.

ing the material to settle, 50 cc. into a beaker. Add 50 cc. of 0.1 N arsenious acid. Stir the mixture well and then titrate back the excess of As_2O_3 with 0.1 N iodine, adding a little starch indicator. Duplicate determinations should always be made. From the amount of As_2O_3 consumed calculate the available Cl in the bleach.

CALCULATION.—1 cc. 0.1 N $As_2O_3 = 0.003546$ gram Cl.

NOTES.—(1) It is generally specified that a good bleaching powder should contain not less than 35% of available chlorine.

(2) A good bleach, when mixed with water in the proportion of 6 parts of bleach to 94 of water and stirred thoroughly for about 20 minutes, should settle clear in not more than an hour.

(3) *Bunsen's Method* for bleaching powder is as follows: Pipette 25 cc. of the bleach solution prepared as above described into a beaker and add an excess of a 10% solution of KI. Dilute to about 100 cc., acidify with dil. HCl and titrate the liberated iodine with 0.1 N thiosulfate, adding a little starch toward the end. The titration gives the amount of available Cl directly. This method, however, is not accurate when calcium chlorate is present, since it liberates the Cl in the latter which is of no value in bleaching. If the amount of chlorate is desired, the difference in chlorine obtained by the two methods represents the chlorine due to chlorate. If the solution is acidified with acetic acid instead of with HCl before titrating, the method gives results comparable with the As_2O_3 method.

(4) Instead of adding an excess of As_2O_3 solution and titrating the excess with iodine, the bleach solution may be titrated directly with the As_2O_3 solution until a drop of the mixture gives no blue stain on starch iodide paper. (Mix starch indicator solution with a few drops of 10% KI solution and soak in the mixture strips of pure filter paper. Use the paper while still damp.)

Bleach Liquor.—Bleach liquor or "Hypochlorite Solution"* is made from bleaching powder by agitating the latter with water, allowing the "mud" to settle and drawing off the clear liquor. The liquor generally used for bleaching rags and wood pulp ranges from 5–8° Bé., corresponding to 20.5–35.5 grams of available chlorine per liter.

Available Chlorine.—For the determination of available chlorine, pipette 10 cc. of the liquor into a 100-cc. volumetric flask, about $\frac{2}{3}$ full of water. Dilute to the mark, mix thoroughly, pipette 10 cc. of this solution into 25 cc. of 0.1 N As_2O_3 solution and titrate the excess of the latter with 0.1 N iodine as described previously. Since the aliquot titrated is equivalent to 1 cc. of

* See also page 42.

the original sample, the number of cc. of 0.1 N As_2O_3 consumed, multiplied by 3.546, will give the available Cl expressed in grams per liter.

NOTE.—The proportions given above are suitable for ordinary bleach liquors. It is necessary, however, in the above procedure that an excess of As_2O_3 be used. On samples whose history is not known, therefore, it is well to make a preliminary titration on 1 cc. of the liquor by the Bunsen method. Have about 5 cc. of 10% KI solution in a beaker, pipette into it 1 cc. of the bleach solution, dilute to about 100 cc., add a few cc. of dil. HCl and titrate the liberated iodine with 0.1 N thiosulfate. From this titration can be calculated the amount of 0.1 N As_2O_3 solution necessary to insure an excess.

REFERENCE.—Sutton: "Handbook of Volumetric Analyses," 10th ed., 177 (1911).

BLEACH CONSUMPTION OF PULP

Weigh accurately 5 grams of the pulp, which should be in the air-dry condition. Cut into pieces about an inch square and place in a suitable container, such as a granite-ware cup, together with sufficient cold water. Thoroughly disintegrate the pulp by means of an egg beater, taking care not to lose any by spattering. The disintegration should not take more than 5 minutes, and should be thorough, or there will be lumps in the test sheets subsequently made.

Transfer the pulp to a funnel containing a perforated porcelain plate, rerunning the first portions passing through, which usually contain a little fiber. Remove excess water with suction. Transfer the pulp to a weighed 6-ounce bottle and add about 25 cc. of water. Then add the requisite number of cc. of standardized bleach solution from a burette. (See Note 1 below.) Place the bottle on the scales and add sufficient distilled water to make the ratio of air-dry pulp to water 1:20. In other words, the weight of the contents of the bottle should be 105 grams, which includes pulp, bleach, and water. Stir the contents thoroughly with a glass rod, stopper the bottle and place in a water bath maintained at 40° C. Let it remain for 4 hours, stirring frequently. Remove the bottle, and filter the contents through the funnel and porcelain plate originally used. Refilter the first runnings if necessary. Wash several times, using suction, and test the contents of the filter flask for bleach by the addition of a crystal of KI. If no yellow color develops, the bleach was completely consumed. If a color shows, add acetic acid, and titrate

the liberated iodine with 0.1 N thiosulfate, using starch. The solution should of course be cool. The back titration, if any, expressed in percentage of bleaching powder should be subtracted from the bleach originally added. Transfer the bleached pulp to a crock or small pan, add a small quantity of water, stir well, and make up hand sheets on a suction mold. Compare these sheets and ascertain the least amount of bleach required to produce a good white.

The strength of the original bleach liquor is determined as follows: Pipette 1 cc. (or an aliquot representing 1 cc.) with a standardized pipette into a flask containing about 50 cc. of water and a few crystals of KI. Acidify strongly with acetic acid and titrate the liberated iodine with 0.1 N thiosulfate. The addition of starch is unnecessary; the end-point can be determined by the disappearance of the yellow color.

1 cc. 0.1 N thiosulfate = 0.00355 gram chlorine. Assuming bleaching powder to contain 33.3% of active chlorine,

1 cc. 0.1 N thiosulfate = 0.01065 gram bleaching powder. Express results as percentage of bleaching powder consumed by the air-dry pulp.

NOTES.—(1) It is highly desirable that 2, or better 3, parallel tests should be carried out simultaneously on the same pulp. Graduated amounts of bleach should be used, say 10, 15, and 20%. If preferred, a single test of 20% of bleach may first be run; and, depending upon the result obtained, 2 or more may be subsequently run, to determine more definitely the bleach required to produce a good white.

(2) It is essential that the pulp density or ratio of pulp to water be always constant. It should be emphasized that results are without value unless all conditions be maintained strictly uniform.

(3) Care should be taken in the making of the test sheets that they be made as nearly the same thickness as possible. It is extremely difficult to compare test sheets for color unless the pressure used in drying (*i.e.*, the surface), density, thickness, and in fact all conditions be carefully regulated.

(4) The assumption of 33⅓% active chlorine in bleaching powder is possibly slightly low. It is customary, however, to take this figure in all our experimental bleaching operations because the amount of chlorine extracted from bleaching powder in ordinary practice is in all cases less than the total available chlorine in the dry powder. With 35% available chlorine in the dry powder, about 33⅓% would be actually present in the pulp mixture.

(5) The above method is the result of experimental work done in this laboratory by R. B. Roe.

CASEIN

General.—Casein is prepared from milk, either by natural souring or by the addition of acid. There are 5 grades of casein: (1) Lactic (natural), (2) Muriatic Pressed, (3) Muriatic Cooked, (4) Sulfuric Pressed, and (5) Sulfuric Cooked. The properties of the different grades are somewhat different, particularly the viscosity in alkaline solution. Grades (3) and (5) have the highest viscosity, grade (2) next, grade (4) next, and grade (1) the lowest. It requires considerable experience to be able to distinguish with certainty between the different grades. Usually a water extract of sulfuric and muriatic caseins will contain sulfates and chlorides, respectively.

Always note the appearance and odor of the sample. A good casein should have a clean, pleasant odor and should be neither moldy, musty, nor rancid. The color should be light yellow or cream color and there should be no dark brown portions or black specks. Bright orange particles indicate that the casein has been burned in drying.

Moisture.—Weigh 5 grams into a shallow porcelain dish and dry to constant weight at 100–105° C. The temperature should not be allowed to run over 105° C.

NOTE.—The moisture is not usually determined in casein. On ground caseins, however, the maximum allowable moisture is generally considered 12%.

Ash.—Weigh 5 grams into a porcelain dish and ignite until the ash is white or grayish white. (Casein must not be ashed in platinum since it attacks this metal.) Cool in a desiccator and weigh.

NOTE.—The ash of naturally soured caseins generally runs between 5 and 8.5%, the ash of acid casein not over 6%. Natural caseins burn to a white ash with greater ease than acid caseins.

Alkali.—Add about 5 cc. of distilled water to the ash and warm. Then add 1 or 2 drops of phenolphthalein indicator. If the ash is alkaline, titrate it with 0.1 N HCl until colorless, then add two drops of methyl orange and complete the titration to a pink color. Calculate to Na_2O.

CALCULATION.—1 cc. 0.1 N HCl = 0.0031 gram Na_2O.

NOTE.—The ash of a pure casein should not be alkaline to phenolphthalein or to methyl orange. If it shows alkalinity, test it qualitatively for borax, sodium carbonate, and sodium phosphate.

Starch (Qualitative Test).—Warm a portion of the sample with distilled water. Cool, and add a few drops of very dilute iodine solution. A blue color indicates starch.

NOTE.—If added alkali has been found in the casein, make the solution slightly acid before adding the iodine solution.

Solubility ("Cutting Test").—Weigh 50 grams of the ground casein into a 350-cc. beaker and add 7.5 grams of powdered borax (equivalent to 15 per cent of the weight of the casein). Add 250 cc. of water at a temperature of 70° C., and heat for 15 minutes at this temperature on the water bath, stirring constantly. High-grade caseins will dissolve completely. Inferior samples will show more or less lumps and mineral impurities. If the lumps are brown or orange color, the casein has probably been burned in preparation. Grit and dirt will settle to the bottom and the approximate amount should be noted.

In carrying out this test always run at the same time a standard high-grade casein for comparison. The Muriatic Flakeless Casein of Innis Speiden and Co.* is a satisfactory standard. Italian casein is also generally a high-grade casein but gives a thinner solution than domestic. Most of the foreign caseins give thinner solutions than domestic caseins.

Clay-carrying Capacity.—Dilute the casein solution obtained above with 250 cc. of hot water. 10 cc. of this solution will then contain 1 gram of casein. Keep the solution hot during use. Weigh out 100 grams of *bone-dry* clay (standard D. Y. coating clay, which has been dried at 105° C., is a suitable clay for this use) and mix thoroughly with 65 cc. of water in a small sauce pan or casserole. When the mixture is perfectly smooth and free from lumps, add 50 cc. of the casein solution. This is equivalent to 5% of casein on the dry weight of the clay. Stir until smooth. Using a paint brush about $\frac{3}{4}$ inch wide, remove a brushful of the mixture and spread it evenly on one end of a strip of paper which should be about 2 feet long and 7–9 inches wide. A smooth-surfaced, fairly heavy wrapping paper is suitable.

*New York City.

Add 10 cc. more of the casein solution to the clay and mix thoroughly. This will make a mixture containing 6% of casein on the weight of the clay. Stir this mixture until smooth and brush on the paper as before. Continue in this manner until mixtures have been made and applied to the paper which contain 5, 6, 7, 8, 9, 10, 11, 12, 13, and 14% of casein, respectively, on the basis of the weight of the clay. Let the coated paper dry overnight at room temperature, or for about 3 hours at 130° F. (55° C.). When dry, determine the "critical clay-carrying point" in the following manner:

Soften a piece of sealing wax by heating until it can be easily worked with the fingers for a distance of 0.5 inch up the stick. A convenient method of accomplishing this is to hold the stick of sealing wax about 0.5 inch above an electric hot plate until soft and then let it cool for about 15 seconds. When this condition is attained, hold the sealing wax 0.5 inch above the hot plate for 15 seconds, remove it and press it down for an instant on the strip of clay-casein coating which contains 5% of casein. Then pull up sharply and observe whether the coating alone comes off or whether some fiber from the sheet adheres to it. Heat the wax as before for 15 seconds, press down on the strip of coating which contains 6% of casein and pull up as before. Repeat until that coating is reached which adheres strongly enough to the paper so that some fibers pull away from the sheet when the wax is pulled up. This is the "critical clay-carrying point." Repeat in the same manner, starting from the 14% casein coating and running down in the opposite direction, in order to check the critical point. If they do not check, the operation should be repeated. Report the Clay-carrying Capacity as the number of parts of clay which 1 part of casein will carry. This is obtained by dividing 100 by the percentage of casein (on the basis of the clay) in the coating where the critical point is found. For example: If the critical point is found in the coating containing 9% casein on the basis of the clay, the clay-carrying capacity is $100 \div 9 = 11.1$.

NOTES.—(1) Always carry out parallel tests on a standard sample of casein for comparison as the kind of clay and the kind of paper both influence the result obtained.

(2) The clay-carrying capacity of a high-grade casein is about 11.

Acidity.—Weigh 20 grams of casein into a casserole, and add 80 cc. of water. Warm, and titrate with 0.5 N NaOH, running in a little at a time with alternate warming on the steam bath until the end-point is reached. Use strips of litmus paper as an outside indicator and apply a drop at a time of the casein solution to the blue paper until the red color is faint. Then apply to both blue and red paper until the end-point is reached. Report the results in terms of cc. of normal caustic solution required to neutralize 1 gram of casein.

NOTES.—(1) This last determination is not usually required.

(2) The tests for solubility and clay-carrying capacity are of especial value in testing casein for use in coating paper.

CLAY

(FOR PAPER MAKING)

General.—Clay or kaolin for use as a filler in high-grade papers or for coating purposes should be pure white and free from artificial bluing. It should not have an appreciably gritty feel when rubbed between the teeth. The best clays will not show more than 1–2% residue by the flotation test nor more than a few tenths of 1% grit (generally less than 0.25%) by the 200-mesh sieve test. They should not contain an excessive amount of free moisture when shipped.

Moisture.—Dry 10 grams to constant weight at 100–105° C. The loss in weight is considered moisture.

Grit.—FLOTATION TEST.—Measure a depth of 2 inches from the bottom of a 500-cc. beaker and make a mark on the beaker to indicate this height. Weigh 20 grams of the clay into the beaker, mix thoroughly with water and fill up to the mark. Let settle for exactly 1 minute and pour off the milky water. Repeat the process until the supernatant water can be poured off practically clear at the end of a minute. Place the beaker on the steam bath until perfectly dry, brush out the settled grit into a balanced watch glass with a camel's-hair brush and weigh it.

200-MESH SIEVE TEST.—Place 10 grams of the clay in a 200-mesh sieve and wash by means of a slow stream of running water and finally with a wash bottle until all the clay has been washed through the sieve. Then wash the residue which does not pass

through into a small beaker, evaporate off the water on the steam bath, brush into a balanced watch glass and weigh accurately.

NOTE.—In both grit tests it is permissible and necessary to break up any lumps of clay with a rubber "policeman," but no hard object should be used for this purpose which might crush particles of the grit. It is well to examine the residues under the microscope.

Color.—Spread out a small amount of the clay, which has been dried at 100–105° C., on white paper by the side of, and in contact with, a similar amount of a (dried) standard sample. Press each down with a spatula to give a smooth surface and compare the color. When the clays are of the same color it is impossible to see any line of demarcation between them. If a permanent record is desired, the color should be measured by a colorimeter or tintometer.

NOTE.—Clays used for coating purposes are generally required to be of a higher degree of whiteness than those used as fillers.

Artificial Coloring.—In 1 of 2 similar white porcelain dishes place a measured amount of freshly prepared, saturated lime water and in the other dish an equal amount of clear, distilled or spring water. Then into each of these liquids dust, from the end of a knife or spatula, a little at a time, equal amounts of clay. If the clay has been artificially blued, the lime water will remove the bluing. After letting stand for a few moments siphon off the excess liquid and examine the moist clay. If the clay has been blued, the residue from the lime-water treatment will show the original color, which will be quite different from the color shown by the moist clay treated with water alone in the other dish.

NOTE.—The so-called "turpentine test" for the presence of artificial bluing in clay is unreliable, since certain natural clays when tested with turpentine behave similarly to those which have been artificially blued.

CROWN FILLER

General.—Crown filler, used as a loading material or paper filler, is a special form of hydrated calcium sulfate.

Total Moisture.—Ignite 2 grams over a Tirrill burner in a platinum crucible for 30 minutes, cool in a desiccator and weigh.

Repeat until no further loss is obtained. The loss in weight is considered the total moisture in the sample.

Combined Moisture.—Calculate the amount of water which will combine with the residue of anhydrous $CaSO_4$, as found above, to form the crystallized form, $CaSO_4 \cdot 2H_2O$, by multiplying the weight of residue by the factor 0.2647, and report on a percentage basis.

Mechanical Moisture.—Subtract the combined moisture from the total moisture to obtain the free or Mechanical Moisture.

NOTE.—This same procedure may also be applied to Gypsum, Terra Alba, Pearl White, Pearl Finish, Alabastine and other calcium sulfate fillers. Color comparisons and grit tests may also be made by the methods previously described under Clay.

GLUE

Moisture.—Weigh 2–3 grams of the glue into a platinum dish, add 10–15 cc. of hot water, mix thoroughly with a small stirring rod and rinse the rod off into the dish with a wash bottle. Evaporate on the steam bath to dryness and then dry to constant weight at 105° C. The loss in weight of the original glue represents the moisture. A good glue normally contains not less than 8% nor more than 16% of moisture. Low moisture may indicate overheating in the manufacture. The moisture content, however, varies with the humidity of the atmosphere.

Ash.—Ignite the above residue in the platinum dish. Use a low heat at first, as too rapid burning will make it very difficult to get rid of the last of the carbon. Then raise the heat and ignite to constant weight at the full heat of a Tirrill burner. Report the residue as Ash.

Note whether the ash fuses or not. If it fuses and its aqueous solution is neutral and contains phosphates and chlorides, the glue is probably made from bone, especially if the ash is over 3%. On the other hand, most hide glues give an ash which does not fuse, owing to traces of lime which render the aqueous solution slightly *alkaline*. The ash may vary from 2 to 8%, according to the quality of the glue. It may also show tests for alum, which is sometimes added to impart a fictitious "body" to glues.

Acidity or Alkalinity.—Dissolve 1 gram of the glue in 500 cc. of distilled water. Add a few drops of phenolphthalein indicator and, if alkaline, titrate with 0.5 N acid. Calculate to Na_2O.

CALCULATION.—1 cc. 0.5 N acid = 0.01550 gram Na_2O.

In case the glue is acid instead of alkaline, titrate the Total Acidity with 0.1 N NaOH and phenolphthalein. It is also sometimes desirable to make a separate determination of the volatile and organic acids in addition to titrating the total acidity. For this determination suspend in a stoppered flask 50 grams of the sample with 80 cc. of cold distilled water for about 10 hours (or overnight). Distill off the volatile acids by means of steam and collect the distillate in a 500-cc. graduated cylinder. After about 100 cc. have distilled add a few drops of phenolphthalein. If the distillate is found to be alkaline, it is not necessary to proceed further with the distillation. Otherwise, when 300 cc. have come over, stop the distillation and titrate the distillate with 0.1 N NaOH and phenolphthalein. This volatile acidity represents HCl and H_2SO_3 and should not exceed 0.2% for a good glue. Report as Volatile Acidity, Calculated as Sulfurous Acid, H_2SO_3.

Subtract from the original titration of the glue the titration required for the volatile acids and calculate the difference as H_2SO_4. Report as Non-volatile Acids Calculated as Sulfuric Acid, H_2SO_4.

CALCULATIONS.—1 cc. 0.1 N NaOH = 0.0041 gram H_2SO_3.
= 0.0049 gram H_2SO_4.

Active Sulfur.—When glue is to be used for sizing anti-tarnish papers, it is desirable to know the amount of active sulfur present, *i.e.*, sulfur in the form of sulfides or sulfites. The determination of this is conducted in exactly the same way as the determination of the Volatile Acidity above described, with the exception that 5 cc. of syrupy H_3PO_4 should be added to the glue solution just before distilling with steam and the distillate should be collected in Br water. After distillation, boil off the Br from the distillate, make acid with a slight amount of HCl and precipitate slowly at boiling temperature with $BaCl_2$ solution. Filter, ignite and weigh the $BaSO_4$ and calculate to SO_2. Report the results as Active Sulfur, Calculated as Sulfur Dioxide.

CALCULATION.—$BaSO_4 \times 0.274 = SO_2$.

Jelly Test.—A very good idea of the value of a single glue sample, or the comparative values of different samples, may be gained by testing the stiffness of the jellies formed. The jellies

from the unknown glues are compared with jellies from the standard varieties of glues as made by the Peter Cooper Glue Factory.* The following grades should be used as standards: No. 1, No. 1–X, No. $1\frac{1}{4}$, No. $1\frac{3}{8}$, No. $1\frac{1}{2}$, No. $1\frac{5}{8}$, No. $1\frac{3}{4}$, and No. 2. The No. 1 is a very high-grade glue and No. 2 a cheap glue. (The Cooper factory also puts out two higher grades than No. 1, namely, No. 1 extra and A extra. Certain other manufacturers also claim to make a glue even superior to A extra.)

The following will give an idea of the relative values of the glues as purchased in large quantities:

	1912 Cents per Pound	1923 Cents per Pound
A Extra	..	32
No. 1	..	28
No. 1X	..	26
No. $1\frac{1}{4}$	14	23
No. $1\frac{5}{8}$	12	$17\frac{1}{2}$
No. $1\frac{3}{4}$	8	$15\frac{1}{2}$
No. 2	6	14

The method to be used in the jelly strength test is as follows: First, decide as to whether the unknown sample is probably a low-grade or a high-grade glue and then select several Cooper standards that will include the grade of the unknown sample. Weigh out 50 grams of each sample of air-dried glue, place in a 300-cc. beaker and add 200 cc. of cold water. Let the glues soak in the cold water until soft throughout. In the case of a ground glue this will require not over 1 hour. In the case of sheet glues, several hours will be necessary. When thoroughly soaked, transfer all the samples at the same time to a steam bath which has been previously regulated. Let the mixtures heat to 160° F. and hold at this temperature until thoroughly dissolved, stirring them from time to time to prevent a skin forming on the top. All the samples should be cooked the same length of time. Fit a 6-inch funnel with cheese-cloth and filter the glue solutions into jelly glasses to within 0.5 inch of the top. Set aside to cool,

* Main works at Gowanda, New York.

taking care that the samples are not disturbed during jellying. In hot weather it is generally necessary to set the glasses in a pan of water to cool them; otherwise the jellies will not be stiff enough for satisfactory tests. This procedure may also be used when results are desired quickly. It is most convenient to cook the samples late in the afternoon and allow them to set overnight.

Place the glasses containing the unknown and standard samples in a row so that the labels cannot be seen. Using the third finger of the left hand, compare the jellies for firmness or strength and rearrange the glasses until the jellies finally stand in order of their firmness. Then examine the labels. The standard samples should, of course, have been arranged in correct order in reference to each other. From the way the unknown samples are distributed among the standard samples they can be rated as to quality. (The grades of glue ordinarily encountered in paper-mill work are those from No. $1\frac{1}{2}$ to No. $1\frac{3}{4}$.)

Report as "Peter Cooper Standard, No. . . . "

Viscosity.—Dissolve 50 grams of the glue in 200 cc. of cold water until soft, as for the Jelly Test. Then warm until dissolved. Determine the number of seconds which is required for a 100-cc. Dudley pipette to deliver its volume of water at approximately 145° F. Heat the water to about 150° F. and fill the pipette somewhat above the mark. Have a rubber tube with a pinch-cock on top of the pipette and by means of the pinch-cock set the water at the mark. Then with a stop watch in the left hand open the pinch-cock *suddenly* and at the same time, start the stop watch. Note the length of time required for the water to run from the upper to the lower mark. Repeat the operation two or three times and take the average. The opening of the pipette should be so adjusted that it will deliver 100 cc. of water in approximately 35 seconds.

Determine the viscosity of the glue solution in the same way, *i.e.*, heat the solution slightly above 145° F.; fill the pipette; set it carefully on the mark and determine the length of time it requires for the glue solution to run from the upper to the lower mark. Run at least 2 determinations and take the average, if they agree reasonably well. Divide this time by the time required for water and report the result as the Specific Viscosity of the glue solution at 145° F.

NOTES.—(1) For viscosity and jelly strength methods adopted by the National Association of Glue Manufacturers see *J. Ind. Eng. Chem.*, **16**, 310 (1924).

(2) The viscosity test runs parallel to the jelly test as shown by the following results obtained on samples of Cooper glues in this laboratory:

Cooper Number	A Extra	1 Extra	1	1X	$1\frac{1}{4}$	$1\frac{3}{8}$	$1\frac{1}{2}$	$1\frac{5}{8}$	$1\frac{3}{8}$	2
Specific Viscosity	4.15	3.40	2.00	1.74	1.50	1.44	1.29	1.26	1.24	1.18

Grease.—Make a strong water solution of aniline blue. Use 25% solutions of the different samples of glue to be tested. To 25 cc. of the glue solution add 2 cc. of the dye, and with a 1.5 inch flat camel's-hair brush draw a smooth streak of the dyed glue across wrapping paper. White spots indicate grease. A comparison of the white spots will indicate the relative amount of grease in the different samples.

The grease may be determined quantitatively by extracting 5–10 grams of the ground and dried material with anhydrous ether in a Soxhlet extractor, evaporating the ether and weighing the residue. It is well to mix the ground sample with an equal volume of ether-extracted sand before placing it in the extraction thimble.

Foam Test.—Use the solution from the viscosity determination for the foam test. Beat it rapidly with a stirring rod or an egg beater for about a minute, then let it stand for 1 minute and note whether an excessive amount of foam remains. Glues which foam badly are objectionable, as air bubbles are likely to get into the joint and thus reduce the area of contact of the glue.

Water Absorption.—Place 10 grams of the sample in small pieces in a weighed beaker and add 200 cc. of water. Place in an ice chest and keep at a temperature of about 40° F. for 24 hours with the beaker covered. Pour off any unabsorbed water and weigh the residue. From the increase in weight of the glue calculate the percentage of water absorbed.

NOTE.—The water absorption is affected by numerous factors such as the temperature of the water, the length of exposure, the amount of free surface of the glue exposed, etc. The test is of some value, however, in comparing different samples. High-grade glues will absorb approximately 10–15 times their weight of water, whereas very weak glues may actually go into solution, forming a thick slime. This test may not give reliable results on finely broken or ground glues.

LIME

(Quicklime)

General.—Lime is the product of the calcination of limestone. As there are many varieties of limestone, the different limes prepared from them will show corresponding variations in composition. Lime consists essentially of CaO or of CaO in natural association with a lesser amount of MgO. It may be divided into 4 types:

1. High Calcium Lime.
2. Calcium Lime.
3. Magnesium Lime.
4. High Magnesium (or Dolomitic) Lime.

There is no sharp dividing line between the different types.

Lime is also often called Quicklime or Burnt Lime to distinguish it from Hydrated Lime which consists essentially of $Ca(OH)_2$ or a mixture of $Ca(OH)_2$, MgO and $Mg(OH)_2$.

Quicklime is generally shipped in 3 forms: (1) lump lime, the sizes coming from the kiln; (2) lump lime screened, which has been forked or screened to remove the portion which will pass a $\frac{1}{2}$-inch sieve; and (3) pulverized lime, quicklime which will pass a $\frac{1}{4}$-inch sieve. Quicklime may also be divided into 2 grades: (A) selected lime, which should be well-burnt lime picked free from ashes, core clinker, or other foreign material; and (B) run of kiln, which should be well-burnt, but is taken without selection.

Quicklime has such a wide range of uses that the type of analysis required on a given sample depends somewhat upon the use for which it is intended. The following method covers the determinations usually made upon high-grade limes. All portions weighed out for analysis should be finely ground and representative of the entire sample.

Specifications.—In Table XIX are given some typical specifications for quicklime for different purposes.

Loss on Ignition.—Ignite 1 gram of the powdered lime in a platinum crucible, gently at first, and then over the blast lamp, until the weight is constant. The loss in weight is moisture and CO_2 and is expressed as Loss on Ignition.

TABLE XIX—SPECIFICATIONS FOR QUICKLIME

A. For cooking rags in paper manufacture (*Am. Soc. Testing Materials* Standard C45–24T).
B. For sulfite pulp manufacture (*Am. Soc. Testing Materials* Standard C46–24T)
C. For structural purposes (*Am. Soc. Testing Materials* Standard C5–24T)
D. For water treatment (*Am. Soc. Testing Materials* Standard C53–24T)
E. For the textile industry (*Am. Soc. Testing Materials* Standard C48–24)
F. For glass manufacture (*Bur. Standards Circ.* 118).

Percentages	*A*	*B**	*C**	*D*	*E**	*F**		
						Grade 1	Grade 2	Grade 3
Calcium lime:								
$CaO+MgO$, minimum	....	....	95	....	....	96	91	83
CaO, minimum	....	94.3	75	....	94	.....	.....	.....
MgO, maximum	....	2.6	....	....	3	.....	.....	.....
$Fe_2O_3+Al_2O_3$, maximum	....	....	....	....	2	.....	.....	.....
Fe_2O_3, maximum	....	....	....	....	....	0.2	0.4	0.8
Al_2O_3, maximum	....	....	....	....	....	3	5	5
SiO_2, maximum	....	....	....	....	2.5†	4	9	17
$SO_3+P_2O_5$, maximum	....	....	....	....	....	1	1	1
CO_2, maximum	....	5	10	....	5	.....	.....	.....
$SiO_2+Al_2O_3+Fe_2O_3$, maximum	....	3.1	5	....	....	.....	.....	.....
Available CaO, minimum	90	....	....	80–90	....	.....	.....	.....
Magnesium lime:								
$CaO+MgO$, minimum	....	....	95	....	....	96	91	83
CaO, minimum	....	56.5	....	....	....	.....	.....	.....
MgO, minimum	....	40.4	20	....	....	.....	.....	.....
Fe_2O_3, maximum	....	....	....	....	....	0.2	0.4	0.8
Al_2O_3, maximum	....	....	....	....	....	3	5	5
SiO_2, maximum	....	....	....	....	....	4	9	17
$SO_3+P_2O_5$, maximum	....	....	....	....	....	1	1	1
CO_2, maximum	....	5	10	....	....	.....	.....	.....
$SiO_2+Al_2O_3+Fe_2O_3$	....	3.1	5	....	....	.....	.....	.....

* The figures given are on the non-volatile basis.
† Silica and insoluble matter.

Acid-insoluble Matter.—Transfer the ignited lime to a beaker and pour over it 50 cc. of water, mix well and add 10–15 cc. of conc.

HCl. Boil for 5 minutes, filter, wash with hot water, ignite and weigh.

NOTES.—(1) *Silica.* The result thus obtained contains most of the SiO_2 and any acid-insoluble silicates. It is the figure usually taken in routine work. If an actual determination of the SiO_2 is desired, evaporate the solution to dryness in a platinum dish as far as possible on the steam bath, then cover and transfer to a hot plate or oven and heat for 1 hour at 200° C., in case of a high-calcium lime, or at 120° C. for a high-magnesium lime. Cool, moisten thoroughly with conc. HCl, let stand a few minutes, add an equal volume of water, cover the dish, and heat on the steam bath for 10–15 minutes. Filter out the SiO_2, wash well with dil. HCl and then twice with cold water. Evaporate the filtrate to dryness, take up with HCl as before and filter through a small paper. Transfer both filters to a weighed platinum crucible, smoke off the paper without flaming and ignite the SiO_2 over a blast to constant weight.

For very accurate work treat the residue in the crucible with 5 cc. of HF and 1 or 2 drops of H_2SO_4, evaporate to dryness and again ignite and weigh. Report the loss in weight by the HF treatment as SiO_2.

(2) For limes containing over 5–10% of acid-insoluble matter it is preferable to fuse 1 gram mixed with about 7 grams of Na_2CO_3 in a platinum crucible till a clear melt is obtained. Then cool the fusion, treat with HCl and determine the silica as in the previous note.

Iron Oxide and Alumina.*—To the filtrate from the previous determination add HCl, if necessary, in sufficient amount to make the total amount equivalent to 10–15 cc. of conc. HCl. Add a few drops of HNO_3 and boil. Dilute to 200-250 cc. Add a very slight excess of NH_4OH and keep just below the boiling point until the odor of NH_3 is barely perceptible. Filter off the iron and aluminum hydroxides while hot, collecting the filtrate in a 250-cc. volumetric flask. Wash with hot water, dry, ignite in a platinum crucible, blast, cool in a desiccator and weigh as $Al_2O_3+Fe_2O_3$.

Iron Oxide.—Fuse the combined $Fe_2O_3+Al_2O_3$ in a platinum crucible with 3–4 grams of $KHSO_4$ at a low temperature. Dissolve in water, add sufficient H_2SO_4 to make a 5% solution and pass through the Jones reductor. Cool and titrate with 0.1 N $KMnO_4$.

* If the silica was purified with HF, fuse the residue from this treatment with a little Na_2CO_3, cool, dissolve in HCl, and add the solution to the second filtrate from the silica determination. (See note 1 above.)

CALCULATION.—1 cc. 0.1 N $KMnO_4$ = 0.008 gram Fe_2O_3.

Alumina.—Subtract the Fe_2O_3 from the combined $Fe_2O_3 + Al_2O_3$.

Lime.—Make the filtrate from the preceding determination up to 250 cc. Mix thoroughly and pipette out 100 cc. into a 350-cc. beaker, heat to boiling and add slowly a boiling solution of 3 grams of $(NH_4)_2C_2O_4$ in water. Continue the boiling 2 or 3 minutes and let the precipitated CaC_2O_4 settle for $\frac{1}{2}$ hour. In the case of magnesium limes, decant through a filter, redissolve the CaC_2O_4 in the beaker and from the filter with HCl, and wash the filter five times with hot water and finally with dil. NH_4OH. Dilute the acid solution to 250 cc., bring to boiling, add a few cc. of $(NH_4)_2C_2O_4$ solution and NH_4OH in slight excess. Boil for 2–3 minutes and set aside for $\frac{1}{2}$ hour. Filter off the CaC_2O_4 on the filter first used, wash thoroughly with small portions of hot water and ignite in a platinum crucible over a Tirrill burner, and finally over a blast lamp to constant weight. Cool in a desiccator and weigh as CaO. Divide this weight by 0.4 and multiply by 100 to obtain the percentage of lime (CaO) in the original sample. Since CaO absorbs moisture from the air, it should be weighed as rapidly as possible.

If the lime contains only a small amount of MgO, one precipitation is sufficient.

NOTES.—(1) If it is desired to complete the analysis in as short a time as possible, a portion of 50 cc. of the filtrate from the $Fe_2O_3 + Al_2O_3$ determination should be precipitated in the usual way with excess of $(NH_4)_2C_2O_4$. Boil for about 5 minutes and let the CaC_2O_4 settle clear. Decant through a qualitative filter and cool (with ice water if possible). Add ammonium phosphate in large excess and 5–10 cc. of conc. NH_4OH. Stir rapidly with a rubber "policeman." From the amount of precipitate thus formed one can judge whether the lime contains sufficient MgO to require a double precipitation or not. For accurate work, if there is more than a slight amount of MgO, a double precipitation should be carried out, using a fresh 100-cc. aliquot.

(2) It is allowable and sometimes preferable to titrate the CaC_2O_4 instead of igniting it. Take a portion of the filtrate from the iron and alumina determination corresponding to 0.2–0.25 gram of the material and precipitate and filter the CaC_2O_4 as above described. In the same beaker in which the precipitation was made place about 125 cc. of water and add 5–7 cc. of conc. H_2SO_4. Drop into this the moist filter paper containing the CaC_2O_4 and heat to about 70° C. Stir to effect decomposition but avoid excessive disintegration of the paper. Titrate the solution with constant

stirring with 0.1 N $KMnO_4$ until a permanent pink color forms. Calculate to CaO.

CALCULATION.—1 cc. 0.1 N $KMnO_4$ = 0.002804 gram CaO.

Magnesia.—Acidify the filtrate from the CaC_2O_4 precipitate (or the combined filtrates, in case of a magnesium lime) with HCl and evaporate until the salts begin to crystallize. Dilute until the salts are again in solution. Add a volume of dil. NH_4OH equal to $\frac{1}{3}$ of the volume of the solution. Chill the solution and add slowly and with constant stirring 2 grams of Na_2HPO_4 or $(NH_4)_2HPO_4$ dissolved in 10 cc. of water. Let stand until completely precipitated. Four hours are usually sufficient, but if possible, it is best to let the solution stand overnight. If the analysis is urgent, stir for $\frac{1}{2}$ hour and the precipitation will be complete. Filter through a weighed Gooch crucible (previously ignited) and wash with a mixture of 1 part dil. NH_4OH (4 : 7), 1 part alcohol and 3 parts water. Dry at 105° C. in the oven. Ignite slowly and finally at the highest heat of the Tirrill burner until the weight is constant, cool in a desiccator and weigh as $Mg_2P_2O_7$.

CALCULATION.—$Mg_2P_2C_7 \times 0.3621 = MgO$.

Divide the weight of MgO by 0.4 and multiply by 100 to obtain the percentage of MgO in the original sample.

NOTE.—The amounts of $(NH_4)_2C_2O_4$ (3 grams) and sodium or ammonium phosphate (2 grams) as given in the procedure are ample to insure complete precipitation of the lime and magnesia.

Carbon Dioxide.—Follow the procedure described under Phosphate Rock on page 775, using a 5-gram sample.

Available Lime.—In using lime to causticize Na_2CO_3 solutions the impurities, including $CaCO_3$, are not available for the reaction and it is often desirable to determine the available CaO. The method is as follows:

Weigh out 1 gram of the sample and add to a little water in a 300-cc. Erlenmeyer flask. Boil for a few minutes until thoroughly disintegrated. Cool and add about 200 cc. of water and 40 grams of granulated sugar. Stopper the flask and mix the contents thoroughly by shaking every 15 minutes or oftener for a period of 2 hours. Filter by suction on a Büchner funnel and wash the residue three times with 10% sugar solution. Titrate the filtrate with 0.5 N HCl and phenolphthalein. Calculate the titration to CaO and report as Available Lime.

CALCULATION.—1 cc. 0.5 N HCl = 0.01402 gram CaO.

NOTE.—For the determination of available lime in milk of lime, use 10 cc. of the sample and omit boiling with water. Otherwise proceed as directed above.

Sulfur Trioxide, Total Sulfur and Phosphoric Anhydride.—See under Limestone, page 434.

HYDRATED LIME

General.—Hydrated lime is a dry powder made by treating quicklime with sufficient water to satisfy its chemical affinity under the conditions of its hydration. When lime is slaked with water, the CaO combines with it but the MgO does not to any great extent (except on long standing). Hydrated lime is therefore essentially $Ca(OH)_2$ or a mixture of $Ca(OH)_2$ with varying amounts of MgO and possibly lesser amounts of $Mg(OH)_2$. It occurs in the same types as quicklime (see p. 426).

Specifications.—In Table XX are given some typical specifications for hydrated lime for different purposes. The specifi-

TABLE XX—SPECIFICATIONS FOR HYDRATED LIME

A. For cooking rags in paper manufacture (*Am. Soc. Testing Materials* Standard C45–24T)
B. For water treatment (*Am. Soc. Testing Materials* Standard C54–24T)
C. For the textile industry (*Am. Soc. Testing Materials* Standard C48–24)
D. Masons' "Hydrated Lime" (*Am. Soc. Testing Materials* Standard C6–24).

Percentages	*A*	*B*	*C**	*D*
CaO+MgO, minimum	....	.....	....	90*
CaO, minimum	....	.....	94	....
MgO, maximum	....	.....	3	....
$Fe_2O_3+Al_2O_3$, maximum	....	.....	2†	....
SiO_2 and insoluble, maximum	....	.....	2.5	....
$Fe_2O_3+Al_2O_3+SiO_2$, maximum	....	.....	....	5
CO_2, maximum	....	.....	7	3
Available CaO, minimum	....	60.5–64.3	....	....
Available $Ca(OH)_2$, minimum	85	80–85	....	....
Fineness test:				
30-mesh residue, maximum	....	.....	....	0.5
200-mesh residue, maximum	....	.....	....	15

* The figures given are on the non-volatile basis.
† Iron in a readily soluble form should be avoided.

cations for hydrated lime for use in the manufacture of glass are the same (on the non-volatile basis) as for quicklime for the same purpose (see Table XIX).

Analysis.—The methods for the chemical analysis of hydrated lime are in general the same as for Quicklime (p. 426). Where the hydrated lime is to be used in structural work, however, the following additional tests should be made:

Pat Test (*Constancy of Volume*)*.—To 20 grams of the sample add 100 grams of standard Ottawa sand (see p. 822). Mix well and add enough water to make a good plastic, but rather dry, mortar. Spread out on a clean glass plate in a layer about $\frac{1}{4}$ inch thick and 4 inches square, of even thickness and not tapering at the edges. If the mortar is too dry to work well, add more water. Place the pat in a closet for 24 hours. Have the temperature of the closet between 65 and 75° F., with a free circulation of air but no draft directly striking the pat. Then soak the pat in water until a film of water stands unabsorbed on its surface. If the pat has cracked at this stage, the consistency of the mortar was too wet and a new pat must be made. (It is well, therefore, to make up 2 or 3 pats at the same time from mortars of slightly different consistencies.)

Next mix 20 grams of the sample with enough water to form a thick cream and spread it in a thin layer on the surface of the pat. After standing for 15 minutes to permit air bubbles to form, trowel to an even surface, making the skim coat as thin as possible without letting the sand show through. Place the pat in the closet, as previously described, for 24 hours; then examine carefully to see that there are no cracks or pops. Suspend in a vessel partly filled with cold water in such a way that the water can boil without touching the pat. Bring the water gradually to boil and keep it boiling gently for 5 hours, the pat being surrounded by steam during this time. Let the water cool for at least 12 hours, remove and examine the pat.

If the steam has no visible effect on the pat, report the sample as "sound." If the pat disintegrates, report as "unsound." If the pat cracks, pops, or shows other minor defects, state the fact but do not report as either sound or unsound.

* *Am. Soc. Testing Materials* Standard C6–24.

Fineness.—Place 100 grams of the sample as received on a No. 30 standard sieve, nested above a No. 200 sieve, and wash with a stream of water from a rubber tube fastened to a faucet. Continue washing until the water coming through the sieves is clear, but not longer than 30 minutes. Dry the residues on both sieves to constant weight at 100–120° C. in a CO_2-free atmosphere. Report the weight in grams retained on the No. 30 sieve as 30-mesh Residue and the sum of both weights as the 200-mesh Residue.

NOTES.—(1) The velocity of the water may be increased by pinching the tubing but should not be sufficient to splash any of the sample out of the sieve.

(2) Do not let water accumulate on the No. 200 sieve. This will clog the openings and prevent completion of the washing within 30 minutes.

(3) Hydrated lime for structural purposes should not show a 30-mesh residue over 0.5% nor a 200-mesh residue over 15%.

Calculations.—Calculate the CO_2 to $CaCO_3$. Subtract the equivalent amount of CaO from the total CaO and calulate the remainder to $Ca(OH)_2$. (This should check the available lime, calculated as $Ca(OH)_2$, if it has been determined.) If the sum of the CO_2 and the H_2O combined as $Ca(OH)_2$ is equal to, or less than, the loss on ignition, there is no unhydrated CaO. Report any excess in the loss on ignition as Free Moisture. If there is insufficient H_2O to combine with the CaO after subtracting the CaO combined as $CaCO_3$, then subtract the CO_2 from the loss on ignition, consider the remainder as H_2O and calculate it to $Ca(OH)_2$. Subtract the CaO as $CaCO_3$ and the CaO as $Ca(OH)_2$ from the total CaO and report the remainder as Free (Unhydrated) Lime.

FACTORS.—$CO_2 \times 2.2743 = CaCO_3$.
$CaCO_3 - CO_2 = CaO$.
$CaO \times 1.3214 = Ca(OH)_2$.
$Ca(OH)_2 - H_2O = CaO$.
$H_2O \times 4.1125 = Ca(OH)_2$.

LIMESTONE

General.—Since limes are made from limestones by burning off the CO_2, the analyses of the two are in general quite similar. For the determination of Loss on Ignition, Acid-insoluble Matter, Iron and Aluminum Oxides, Silica, Lime, Magnesia and Carbon

Dioxide follow the same procedures as given above in the method for Lime. A 1-gram sample is sufficient for the CO_2 determination. For routine analyses the CO_2 may be determined in an alkalimeter as described under White Lead on page 274.

For certain purposes additional determinations are required as described below.

Phosphorus.—Dissolve 10 grams of the sample in 80 cc. of dil. HNO_3 (1:1), filter and wash the residue with hot water. Ignite the residue, fuse it with a little Na_2CO_3, cool, dissolve in HNO_3 and add to the main filtrate. Boil the acid solution with 10 cc. of a 1.5% solution of $KMnO_4$ until MnO_2 is precipitated. Dissolve the latter by adding H_2SO_3 or a sulfite free from P, and boil to expel oxides of N and S. Neutralize with NH_4OH, add 1 cc. of conc. HNO_3 for each 100 cc. of solution and complete the determination by the molybdate method as described on page 138.

NOTE.—If the sample contains clay or considerable acid-insoluble material, mix 10 grams, finely powdered, with 5 grams of Na_2CO_3 and fuse over a blast lamp in a platinum crucible. Dissolve the cooled fusion in HNO_3 and evaporate to dryness. Take up the residue with dil. HNO_3 (1:2), filter and wash with hot water. Ignite the residue in a platinum crucible and evaporate with HF and HNO_3. Finally evaporate twice to dryness with HNO_3 to remove all F, dissolve the residue in HNO_3, add to the main filtrate and proceed as above.

Sulfur Trioxide.—Weigh 2 grams of the powdered sample in a small beaker and stir with 10 cc. of cold water until all lumps are broken up and the lighter particles are in suspension. Add 15 cc. of dil. HCl and heat until reaction ceases. Filter and wash thoroughly with hot water. Dilute the filtrate to 250 cc., heat to boiling and add 10 cc. of a boiling 10% solution of $BaCl_2$, drop by drop with constant stirring. Boil for $\frac{1}{2}$ hour or let stand overnight. Filter, wash with hot water, ignite, cool in a desiccator and weigh as $BaSO_4$. Calculate to SO_3, or if desired to $CaSO_4$.

CALCULATIONS.—$BaSO_4 \times 0.3430 = SO_3$.

$BaSO_4 \times 0.5832 = CaSO_4$.

Total Sulfur.—Digest 2 grams of the powdered sample with 25–30 cc. of Br water on the hot plate for 15 minutes. Add 15 cc. of dil. HCl (1 : 1) and boil until action ceases and all Br has

been expelled. Then proceed as above under Sulfur Trioxide. Calculate to S.

CALCULATION.—$BaSO_4 \times 0.1373 = S$.

Final Calculations.—For routine analyses calculate the CaO and the MgO to carbonates. Subtract the equivalent amount of CO_2 from the loss on ignition and report the difference as Moisture and Volatile Impurities.

CALCULATIONS.—$CaO \times 1.7847 = CaCO_3$.
$MgO \times 2.0915 = MgCO_3$.

NOTE.—*Free Moisture.* If an actual determination of free moisture is desired heat 1 gram of the sample at 120° C. for 2 hours in a tared, low form, flat-bottomed, weighing bottle. Stopper quickly and cool in a desiccator. Then lift the stopper momentarily and weigh. Report the loss in weight as Free or Mechanical Moisture (loss at 120° C.).

ROSIN

General.—Rosin is graded according to color. The grades are as follows: WW, WG, N, M, K, I, H, G, F, E, D and B. The WW is the best and palest grade. B is the cheapest and darkest grade. Grades G, F, and E are most frequently used for paper making. Yaryan Extract Rosin grades between E and F and is ruby red in color.

Grade.—To determine the grade of rosin a set of standard cubes of rosin of the various grades must be available.* The rosin under test is cast into a cube in a mold of sheet aluminum and compared as to color with the standards by looking through the cubes toward the light. Care must be taken to heat the rosin only just enough to pour, since overheating darkens the color.

Dirt and Foreign Matter.—Unless the rosin is quite dirty, no quantitative estimation is necessary. In case a quantitative estimation is desired, dissolve 25 grams of rosin in warm alcohol; filter through a tared filter paper; wash with alcohol, dry and weigh the residue.

Saponification Number.—Weigh 2 grams of powdered rosin into an Erlenmeyer flask of 300-cc. capacity. Add 25 cc. of 0.5 N alcoholic KOH and boil for 2 hours under a reflux condenser. Shake the flask frequently with a swirling motion to prevent the

* These may be obtained from D. C. Campbell, Jacksonville, Fla.

rosin from sticking to the sides of the flask above the liquor line. Cool and titrate the excess KOH with 0.5 N acid and phenolphthalein. Calculate the milligrams of KOH consumed per gram of rosin. This is the Saponification Number. In each case run a blank on the KOH solution by boiling 25 cc. of the solution for 2 hours and titrating in exactly the same manner that the saponification proper is carried out.

CALCULATION.—1 cc. 0.5 N KOH = 28.05 mg.

Acid Number.—Dissolve 1 gram of powdered rosin in warm alcohol (neutral to phenolphthalein); cool and titrate the solution with 0.5 N NaOH, using phenolphthalein. Express the result as milligrams of KOH consumed per gram of rosin. This is the Acid Number. It is sometimes customary to report the percentage of acid. This should be calculated as abietic acid.

CALCULATION.—1 cc. 0.5 N NaOH = 0.1511 gram abietic acid.

Ester Number.—The ester number is the difference between the saponification number and the acid number.

Unsaponifiable Matter. (*a*) *In Alcoholic Solution.*—Saponify about 5 grams of the rosin by boiling for 2 hours under a reflux condenser with an excess of 0.5 N alcoholic KOH. Evaporate most of the alcohol, add about 100 cc. of water and extract in a separatory funnel with acid-free ether exactly as in the determination of Free Rosin in Rosin Size (p. 437).

(*b*) *In Aqueous Solution.*—Saponify about 5 grams of the rosin by boiling for 4 hours under a reflux condenser with 1 gram of Na_2CO_3 dissolved in 50–75 cc. of water. Cool the solution and extract in a separatory funnel with acid-free ether as above.

NOTE.—The rosin unsaponifiable in aqueous solution represents more nearly the rosin which is unacted upon in determining the acid number and, since rosin size is made with soda ash, it is considered to be the unsaponifiable matter so far as size-making purposes are concerned.

Ash.—The determination of ash is seldom necessary. It is accomplished by igniting 5 grams in a platinum crucible to a white or light gray residue. Cool in a desiccator and weigh.

Practical Sizing Tests of Rosin.—It is sometimes desirable to make a practical sizing test of rosin in comparison with a rosin which is regarded as standard. For this purpose a small beating engine is desirable, although the work can be done by using a

cream whipper. Thoroughly disintegrate 25 or 50 grams (dry weight) of unbleached sulfite pulp in the beater or cream whipper and add 2% of rosin size in the form of a thin milk. After thorough mixing add 3% of a standard alum dissolved in water and again thoroughly mix. The pulp is then thinned, made into hand sheets and the dried sheets are tested for ink penetration (p. 471). Make two sets of sheets, one with size made from a standard rosin and the other with size made from the rosin under test. The size is made by cooking a given weight of powdered rosin, in a container surrounded by boiling water, for 4 hours with that weight of soda ash (Na_2CO_3) which will yield a size containing 25% free rosin on the dry basis, *i.e.*, with sufficient Na_2CO_3 to neutralize 75% of the free acid in the rosin. The water used in making up the size should be sufficient to give a finished thick size containing 30% dry matter. The thick size is diluted to a milk by stirring with water at 70° F. before adding to the pulp.

ROSIN SIZE AND ROSIN SIZE MILK

General.—Rosin size consists essentially of a mixture of rosin-sodium soap with free rosin and more or less water. Thick, viscous sizes generally contain from 25–50% of water and hard, dry sizes from 1–10% of water. For paper mill use they are very much diluted with water and used in the form of rosin size milk, which may contain anywhere from 80–99% of water (usually about 98%).

Rosin size hydrolizes more or less on dilution with water. It is therefore necessary in determining the free rosin to keep the volume of water as small as possible and for consistent results directions should be followed exactly. We have found in many instances that when a rosin size is diluted down to a milk, the analysis of the milk will give more free rosin, calculated to the dry basis, than the analysis of the original size shows on the dry basis.

Rosin Size

Free Rosin.—Weigh out accurately about 10 grams of size and mix with 30 cc. of water. (With solid or dry size, 6–8 grams will be sufficient.) Wash with as little water as possible into a 250-cc.

separatory funnel, free from any trace of acid or alkali. Extract with 25 cc. of *acid-free* ether. If an emulsion forms, add about 10 cc. of neutral alcohol and shake the mixture. Draw off the watery layer into a second sparatory funnel, extract this with a second portion of *acid-free* ether and add the ether extract to that in the first funnel. Wash the combined ether extracts with two 25-cc. portions of water, adding the wash waters to the solution in the other funnel. Pour the washed ether extract into a weighed Soxhlet flask. Finally extract the water solution a third time with 25 cc. of ether, first using the ether to rinse out the funnel which contained the ether extracts. Draw off the watery layer into another separatory funnel, wash the third ether extract twice with 25-cc. portions of water. Draw off the water each time into the funnel containing the soap solution. Pour the washed ether extract into the Soxhlet flask containing the main ether extract. Distill off the ether and dry the flask at not over 105° C. to constant weight. Cool in a desiccator and weigh the free rosin.

NOTES.—(1) It is especially important that all ether used in this determination shall have been specially prepared by washing once with Na_2CO_3 solution and then several times with water. It should be tested with a *moist* piece of sensitive blue litmus paper, which should not change color when completely submerged in it for 15 minutes.

(2) A convenient way to distill off ether is to connect the flask with a Soxhlet extractor and distill the ether up into the extractor.

Moisture.—Run the residue from the free rosin determination into a 250-cc. volumetric flask (or a 500-cc. flask if necessary). Dilute to the mark and mix thoroughly. Pipette an aliquot equivalent to $\frac{1}{10}$ of this solution into a weighed platinum dish, evaporate to dryness on the water bath, and then dry at 105° C. to constant weight. Two hours' drying ought to be sufficient. Divide this weight by $\frac{1}{10}$ of the weight of the sample taken and multiply by 100. This gives the percentage of dry matter in the size, exclusive of free rosin. Add the percentage of free rosin as above determined, and subtract the sum from 100; the difference will be the percentage of water.

Ash and Total Alkali.—Ignite the residue from the moisture determination until all carbonaceous matter is burned off. Dry in a desiccator and weigh. Dissolve the residue in a few cc. of

water and titrate with 0.1 N acid and methyl orange. Calculate the titration directly to Na_2CO_3. This weight should check the weight of ash reasonably closely, unless the size contains insoluble or other foreign matter. Calculate the titration also to Na_2O; divide the weight thus obtained by $\frac{1}{10}$ of the original sample taken, and multiply by 100. This gives the percentage of Na_2O in the size.

CALCULATION.—1 cc. 0.1 N acid = 0.0031 gram Na_2O.
= 0.0053 gram Na_2CO_3.

Combined Rosin.—Pipette an aliquot representing $\frac{4}{5}$ of the soap solution from the determination of free rosin into a separatory funnel and acidify with 10 cc. of dil. H_2SO_4 (1:5). Add 25 cc. of ether, shake well and let stand until the 2 layers are completely separated. Draw off the water solution into the second separatory funnel and wash the ether with two 25-cc. portions of water, drawing off the water into the second funnel and pouring the ether extract into a weighed Soxhlet flask. Rinse the first funnel with 25 cc. of ether into the second funnel. Shake well and draw off the water layer into the first funnel. Wash as above with two 25-cc. portions of water. Repeat once more. Evaporate the ether from the combined extracts as in the free rosin determination. Dry to constant weight at not over 105° C. Divide the weight obtained by 0.8 of the original weight of sample taken and multiply by 100 to obtain the percentage of combined rosin.

NOTES.—(1) The ether in this case does not need to be specially purified, though it should be free from any non-volatile residue.

(2) The combined rosin thus obtained is weighed as rosin acids, whereas in the combined state it is actually present as anhydride. There are usually slight losses in manipulation and it is customary to report the combined rosin as actually weighed. Since rosin anhydride = rosin acid × 0.97, the usual rosin analysis should add up somewhat over 100%, depending upon the amount of combined rosin present.

Free Carbonate.—Weigh out 10 grams of size and dissolve in 200 cc. of *acid-free* absolute alcohol. Let the solution stand 8–10 hours, or overnight if possible, protected from acid fumes and moisture. Filter on a weighed dry filter and wash thoroughly with absolute alcohol. Discard the alcoholic solutions. Pour

boiling water through the filter, and after cooling, titrate the aqueous solution with 0.1 N acid and methyl orange. Calculate to Na_2CO_3.

CALCULATION.—1 cc. 0.1 N acid = 0.0053 gram Na_2CO_3.

NOTES.—(1) The filter need not be weighed if the Insoluble Matter is not to be determined. (See below.)

(2) The determination of free alkali by this method is subject to a slight error on account of the solubility of Na_2CO_3 in alcohol. Tests made in this laboratory show that when 0.5 gram of anhydrous Na_2CO_3 was allowed to stand 16 hours in 200 cc. of 95% alcohol, 0.0075 gram went into solution. In the case of absolute alcohol 0.0050 gram dissolved. With 10 grams of ordinary rosin size and 200 cc. of absolute alcohol, the moisture in the size dilutes the alcohol to about 95% and the solubility of Na_2CO_3 would cause results about 0.07% too low. Consequently, this figure may be used as a positive correction where greater accuracy is desired.

Insoluble Matter.—Any insoluble matter will be left on the weighed filter in the above determination of free Na_2CO_3 and may be dried and weighed. In order also to determine whether this is mineral matter, it may be ignited and the mineral matter weighed.

ROSIN SIZE MILK

Specific Gravity.—Take the sp. gr. with a pycnometer at a definite temperature; and for the various determinations pipette out definite volumes of the sample at the same temperature.

Total Solids.—Pipette 100 cc. into a weighed platinum dish, evaporate to dryness, then dry to constant weight at 105° C., cool in a desiccator and weigh.

Total Alkali.—Ignite the residue from the moisture determination above and titrate with 0.1 N or 0.01 N acid and methyl orange (see Total Alkali under Rosin Size above).

Total Free Rosin.—Pipette 100 cc. into a separatory funnel and extract with 50–75 cc. of *acid-free* ether without excessive shaking (see Free Rosin under Rosin Size above).

NOTE.—If difficulty is experienced from emulsions, add 5–10 cc. of neutral ethyl alcohol, or very cautiously apply suction to the top of the separatory funnel by means of a cork stopper with a glass tube running through it.

Inert Free Rosin.—If the milk appears to contain suspended rosin which settles on standing, boil 300 cc. for 30 minutes,

filter on a filter paper which has been dried at 100° C. and weighed in a stoppered weighing bottle, wash with hot water and weigh the dried residue.

Total Rosin.—Pipette 50 cc. of the milk into a separatory funnel, add 10 cc. of very dilute H_2SO_4 (1%), then 50 cc. of ether and proceed as under Combined Rosin described above under Rosin Size.

Combined Rosin.—Subtract the total free rosin from the total rosin and report the difference as Combined Rosin.

SATIN WHITE

General.—Satin White is a paste composed of water, aluminum hydroxide, calcium hydroxide and hydrated calcium sulfate, and is made by adding an excess of milk of lime to a solution of alum.

Aluminum Hydroxide.—Weigh out rapidly 10 grams of the paste; dissolve in dil. HCl and hot water. If any insoluble matter remains after boiling, it should be filtered out, ignited, and weighed. Make the filtrate up to 500 cc. in a volumetric flask and pipette 50 cc. into a beaker. Make slightly ammoniacal, heat to boiling, filter out the $Al(OH)_3$, wash thoroughly with hot water, ignite over a Tirrill burner and then in the blast lamp and weigh as Al_2O_3. Calculate this to $Al(OH)_3$.

CALCULATION.—$Al_2O_3 \times 1.5301 = Al(OH)_3$.

Total Lime.—Heat the filtrate from the $Al(OH)_3$ determination to boiling and add a slight excess of $(NH_4)_2C_2O_4$ solution. Let settle, filter, wash with hot water, ignite in the blast lamp and weigh as CaO.

NOTE.—If preferred, the CaC_2O_4 precipitate may be titrated with 0.1 N $KMnO_4$ (see p. 429).

Calcium Sulfate.—Pipette 50 cc. of the original solution into a beaker, dilute with 100 cc. of water, and heat to boiling. Then add, drop by drop, a slight excess of boiling $BaCl_2$ solution and boil for 5 minutes. Let stand overnight. Filter out the $BaSO_4$, wash with hot water, ignite and weigh as usual.

Calculate the $BaSO_4$ to $CaSO_4 \cdot 2H_2O$, subtract the CaO equivalent of this from the total CaO, and calculate the remainder to $Ca(OH)_2$.

CALCULATIONS.—$BaSO_4 \times 0.7376 = CaSO_4 \cdot 2H_2O$.
$BaSO_4 \times 0.3430 = SO_3$.
$CaSO_4 \cdot 2H_2O \times 0.3257 = CaO$.
$CaO \times 1.3214 = Ca(OH)_2$.
$SO_3 \times 2.1504 = CaSO_4 \cdot 2H_2O$.

Moisture.—It is generally customary to take the moisture "by difference." Add together the percentages of insoluble matter, $Al(OH)_3$, $CaSO_4 \cdot 2H_2O$ and $Ca(OH)_2$, and subtract the sum from 100, reporting the difference as Moisture.

NOTES.—(1) The moisture cannot be accurately determined by direct drying at 105° C. because the $CaSO_4 \cdot 2H_2O$ loses some of its water of crystallization on heating. If desired, the total loss on ignition may be determined and the uncombined water calculated from this. For accurate results it is necessary to use the blast lamp to make sure all the combined water is driven off.

CALCULATIONS:

Combined H_2O from $CaSO_4 \cdot 2H_2O = CaSO_4 \cdot 2H_2O \times 0.2093$.
Combined H_2O from $Al(OH)_3 = Al(OH)_3 \times 0.3465$.
Combined H_2O from $Ca(OH)_2 = Ca(OH)_2 \times 0.2432$.

(2) If any $CaCO_3$ is present, as is sometimes the case when Satin White is made from "lime mud," it is, of course, necessary to determine the amount of CO_2 present and take this into account in making the calculations.

CALCULATION.—$CO_2 \times 2.2743 = CaCO_3$.

(3) There is a patented coating material on the market known as Rafold, which is in general similar to satin white except that it is made from dolomitic lime and therefor contains considerable magnesia.

TALC

(FOR PAPER FILLER)

General.—Pure talc is a hydrated magnesium silicate. The commercial article, however, is generally a double silicate of Mg and Al in which the Mg predominates. It contains, as natural impurities, Fe_2O_3, $CaCO_3$, and sand. The $CaCO_3$ is due to the difficulty in separating the talc from the limestone in which it occurs. For use as a paper filler, talc should show an analysis within the following limits:

Sp. gr.	2.7–2.9
$CaCO_3$	Not over 4%
Fe_2O_3	Not over 2%.

Talcs containing up to 10% of $CaCO_3$ are not necessarily adulterated, but if they contain more than 4% can only be used for cheap packing paper and pasteboard.

Loss on Ignition.—Weigh 1 gram in a platinum crucible, ignite at bright red heat to constant weight and calculate the loss in weight. For normal talc this is about 4%.

Calcium Carbonate.—Place 1 gram in 400 cc. of water and add about 2.5–3 cc. of conc. HCl. Boil gently for 15–20 minutes; filter and wash. To the filtrate, add 10 cc. of conc. HCl, then make slightly ammoniacal, boil and filter out any $Al(OH)_3$ which may precipitate. To the filtrate add $(NH_4)_2C_2O_4$ solution in excess; and after the precipitate has settled, filter, wash with hot water, ignite over the blast and weigh as CaO. Calculate to $CaCO_3$.

CALCULATION.—$CaO \times 1.7847 = CaCO_3$.

Iron Oxide.—Weigh 1–2 grams in a large platinum crucible, add a few drops of dil. H_2SO_4 and evaporate 2 or 3 times with 10–15 cc. of HF. Then fuse the residue with anhydrous $KHSO_4$. Dissolve in water and filter if necessary. Add sufficient H_2SO_4 to make a 5% solution, and run through the Jones reductor. Cool and titrate immediately with 0.1 N $KMnO_4$.

CALCULATION.—1 cc. 0.1 N $KMnO_4 = 0.008$ gram Fe_2O_3.

Specific Gravity.—Fill a 200-cc. beaker about $\frac{2}{3}$ full of xylene (commercial xylol). Bend a fine platinum or steel wire around a platinum crucible in such a way that it may be suspended from the hook above the balance pan. Weigh the crucible completely submerged in the xylene. From a weighing bottle partly filled with the talc, and previously accurately weighed, pour into the crucible (which should be about half full of xylene) approximately 1 gram of the talc, very slowly and carefully, to avoid loss through any of the powder being blown away. Tap the crucible gently to dislodge any air bubbles. Again submerge and weigh in xylene. The increase in weight represents the weight of the talc in xylene. The weight of talc is obtained by again weighing the weighing bottle. The difference between the weight of talc in air and in xylene represents the weight of xylene displaced. Determine the sp. gr. of the xylene in the beaker immediately with the Westphal balance. Calculate the result from the formula:

$$\text{Sp. gr. of talc} = \frac{\text{Wt. of talc taken}}{\text{Wt. of xylene displaced}} \times \text{sp. gr. of xylene.}$$

NOTE.—Talc is often adulterated with barytes and with feldspar and if the sp. gr. of the talc is above 2.9, it indicates that the talc is adulterated with some heavy material such as these.

Gypsum.—Boil 2 grams in a beaker with 25 cc. of dil. HCl (1 : 4) and filter into a 250-cc. volumetric flask, washing the residue thoroughly with hot water. Cool the filtrate and dilute to the mark. Test about 100 cc. of this solution with $BaCl_2$. If it gives an appreciable precipitate, the amount should be determined. For this purpose heat to boiling an aliquot of 100 cc. and add a boiling solution of 10 cc. of 10% $BaCl_2$ solution a drop at a time. Boil for 30 minutes, let stand until clear and filter out the $BaSO_4$. Wash, ignite, and weigh. Calculate to gypsum.

CALCULATION.—$BaSO_4 \times 0.7376 = CaSO_4 \cdot 2H_2O$.

NOTE.—The amount of CaO present as gypsum should be subtracted from the total CaO as previously determined before calculating to $CaCO_3$.

$$CaSO_4 \cdot 2H_2O \times 0.3257 = CaO.$$

Grit.—A good idea of the relative amount of grit in two samples can be obtained by placing alternately portions of one and then the other on the tongue and rubbing the talc between the teeth. Quantitative estimation is carried out by means of the flotation test and the 200-mesh sieve test as described in the method for Clay (p. 419).

REFERENCE.—*Paper*, **6**, No. 4, 13 (1912).

ULTRAMARINE

Strength of Color.—Weigh out 1 gram of the ultramarine and 10 grams of barytes ($BaSO_4$) in a 1-ounce bottle together with some small, round lead shot and agitate until a uniform mixture is obtained, using great care not to get any of the ultramarine on the stopper until it is fairly well mixed with barytes. This can be accomplished by giving the bottle a rotating motion at first. Then take out a little of the mixture with a spatula and spread it upon a piece of white paper beside a similar portion of the standard with which the comparison is made.

A series of standards should be made up in a similar manner, mixing with 10 grams of $BaSO_4$ the following amounts, respectively, of standard ultramarine: 0.70, 0.75, 0.80, 0.85, 0.90, 0.95, 1.00, 1.05 and 1.10 grams.

In reporting the results state whether the sample is stronger or weaker than the standard and give the parts of sample equivalent to 1 part of the standard.

NOTE.—It is important that the same barytes should be used for the standard as for the sample under examination and it should be dried before weighing.

Resistance to Alum.—Weigh 0.2 gram of the sample into a test-tube and add 10 cc. of a 10% solution of alum.* Shake for about 1 minute, then allow it to stand with an occasional shaking. Treat the standard ultramarine in a similar manner and compare with the sample under examination. Some ultramarines are decomposed by alum, resulting in a decided weakening of the shade.

NOTE.—In some instances, if the ultramarine is very resistant, it is necesary to warm the solution very slightly.

Shade.—Ultramarine should be tested for shade by comparing the sample and the standard undiluted, since with dilution the shade appears dull.

FIBERS IN PAPER

Quantitative Estimation.—Tear small bits from different portions of the sample, using in all 1 or 2 square inches. Tear these pieces into smaller pieces about $\frac{3}{16}$ to $\frac{1}{4}$ inch square and place in a test-tube about $\frac{1}{3}$ filled with 0.5% NaOH solution. Boil briskly for a few moments. Fill the test-tube with cold water and decant off the liquid. Then fill it with 0.5% HCl once and several times with cold water, decanting off the liquid each time. Finally fill the tube completely with water and invert on the palm of the hand. By raising the edge of the tube cautiously, allow all the water to drain out, leaving the pieces of paper in the hand. Roll these into a hard ball between the thumb and finger and return to the test-tube. Make sure that all the HCl has been washed out of the paper fibers. Fill the tube about $\frac{1}{3}$ full of water and shake vigorously. This should completely disintegrate the fibers, making a uniform suspension.

* Paper-makers' alum, $Al_2(SO_4)_3 \cdot 18H_2O$.

NOTE.—Parchment papers are very difficult to prepare for fiber analysis. The following procedure is recommended:

Pour conc. H_2SO_4 into an equal volume of water and warm 50 cc. of the solution in a beaker to 50–60° C. Place in it pieces of the parchment and, as soon as they begin to soften, beat them up vigorously with a glass rod. Pour the pulp on a Gooch crucible with fine holes and wash well with water. Then roll into a ball and shake up with water as above. The operation must be carried out as rapidly as possible before the more delicate wood fibers are excessively attacked by the hot acid. In the case of true parchment papers (100% rag) the danger of excessive treatment is minimized.

Remove a portion of the suspended fibers on the end of a microscope needle and blot off the excess moisture on a clean filter paper, holding the needle horizontally and making sure that the point does not remove any fibers from the filter paper. Place the fibers on a clean glass microscope slide and add 2 drops of Herzberg's fiber stain (see notes). Pull the fibers apart, using 2 clean needles, until a uniform mixture is obtained, free from any lumps or clots of fibers. Place a clean cover-glass over the fibers, press down very gently with the needles and withdraw the excess liquid about the slide with a clean filter paper. (Do not attempt to press out all the liquid. A good slide should have a film of liquid between the glasses and should be free from air bubbles.) The slide is then ready for microscopical examination.

For microscopical examination a magnification of about 100 diameters is desirable. An 18-mm. ($\frac{3}{4}$-inch) objective and a 25-mm. (1-inch) eye-piece make a satisfactory combination. In general, the different fibers used in paper are colored by the stain as follows:

Rag (cotton, linen, hemp): pale red to brownish- or purplish-red.

Bleached chemical wood (sulfite, soda, etc.):* deep blue.

Ground wood: bright yellow, sometimes pale yellow.

Jute and manila: vary all the way from blue through violet and red violet to brownish-yellow and greenish-yellow.

Straw and esparto: generally dark blue, but sometimes reddish or yellowish.

For the characteristics of the different fibers the standard books should be consulted; particularly good illustrations and

* So-called "alpha cellulose" made from sulfite pulp behaves the same as ordinary sulfite.

descriptions are given in Herzberg's "Papier-prüfung," 3d ed. (pp. 88 and 89, and tables in the back of the book).

In estimating the amounts of the various constituents, standard slides should be prepared from papers of known composition (p. 452), and frequently compared with the samples under examination. No account is taken of the amount of filler or sizing materials that may be in the paper; the fiber estimate is based on the relative proportions of the different fibers, considering the total fiber content as 100%.

NOTES.—(1) *Herzberg's Stain* is made up as follows:

Solution A.—20 grams anhydrous $ZnCl_2$, 10 cc. water.

Solution B.—2.1 grams KI crystals, 0.1 gram iodine crystals, 5 cc. water.

Cool each solution and mix slowly, keeping cool. Let the precipitate settle overnight and pour off the supernatant liquid, or filter through glass wool. Add a small flake of iodine and preserve the stain away from the light or in a colored glass bottle. The stain should be allowed to stand a day or two before using.

(2) It is sometimes difficult to obtain satisfactory $ZnCl_2$. In such cases the following alternative formula may be used for the stain: 25 cc. of saturated $ZnCl_2$ solution, 5.25 grams of KI, 0.25 gram of iodine, and 12.5 grams of water. By mixing the ingredients as stated above the proper stain can be obtained at once.

(3) The Bureau of Standards* recommends the following standard formula:

Solution A.—50 grams dry $ZnCl_2$ (fused sticks); 25 cc. of water added from a pipette into the $ZnCl_2$ bottle, stoppered and shaken. This should give about 40 cc. of solution. Take the sp. gr. at 28° C. If necessary add water from a 1-cc. pipette until the sp. gr. is 1.8, then pour into a tall cylinder.

Solution B.—Measure 12.5 cc. of water. Use part to rinse the thermometer, hydrometer, and original $ZnCl_2$ bottle and add to Solution *A*. In the balance of the water dissolve 5.25 grams of KI and 0.25 gram of I_2.

Add *B* to *A*, stir well and place in the dark. The following day pipette off the clear portion into a black bottle, leaving 3–4 cc. of the solution above the sediment. The stain will be found to be satisfactory for at least 2 weeks. Weights and measures must be observed carefully.

(4) It is very important to have satisfactory stain, otherwise results will be worthless. To test out the stain, prepare a microscope slide from a mixture of about equal parts of bleached soda and sulfite and rag fibers. If the stain is correct, the soda should show a dark blue, the sulfite a lighter blue, and the rag a red or wine-red color. If the blue color is more of a violet, then too much iodine is present and more water or $ZnCl_2$ should be added. $ZnCl_2$ produces the blue color, iodine produces the red and yellow

* Muriel F. Merritt: *Paper Trade J.*, Aug. 24, 1922.

colors and the addition of water serves to weaken the color which predominates.

It is advisable to have a separate stain for use on papers containing ground wood, so adjusted that it will give a bright lemon-yellow on a standard ground-wood pulp and a slightly greenish-blue on unbleached sulfite.

(5) We have found in certain cases where papers are made from two or more fibers of widely varying length, such as ground wood and a high-grade sulfite, there is a tendency for the short fibers to settle out and if the mixture in the test-tube is removed with a microscope needle, too great a proportion of the long fibers will be obtained. In such cases the test-tube should be very vigorously shaken and a drop or two of the mixture quickly poured out on a hard filter paper. In such cases also care should be taken not to use more stain than is necessary as there is danger when the cover-glass is pressed down that the short fibers will be squeezed out around the edges.

Distinction between Sulfate (Kraft) and Unbleached Sulfite.* The Herzberg Stain will not differentiate sulfate or kraft fibers from sulfite. It has been found, however, that fairly satisfactory results can be obtained on mixtures of sulfate and unbleached sulfite by using a stain consisting of a mixture of 1 part of a 2% solution of malachite-green and 2 parts of a 1% solution of basic fuchsin or magenta. The solution should be made up according to the following formulas, kept in tightly stoppered bottles and mixed only when wanted for use:

(*a*) Dissolve 2 grams of malachite-green hydrochloride in 100 cc. of water.

(*b*) Dissolve 1 gram of basic fuchsin hydrochloride in 100 cc. of water.

As dyes and stains from different sources are not exactly the same, it is necessary to test out the stain after it has been made up, on samples of sulfite and sulfate fibers. Shake up authentic samples of unbleached sulfite and sulfate and place on a slide a few fibers of each, taking care not to get the two samples mixed. Then dry the fibers, stain as directed below, and examine microscopically. All the *sulfate* fibers should have a *blue*† or *blue-green* color and all the *sulfite* fibers should have a *purple* or *lavender* color. If any purple fibers appear in the sulfate pulp, this indicates that too much fuchsin is present in the combination and a little more malachite-green must be added to counteract this effect. If some of the sulfite fibers show green or blue, there

* *Bur. Standards Tech. Paper*, 189 (1921).

† Ground wood also stains blue with this treatment.

is too much malachite-green in the combination and more fuchsin solution must be added.

The stain should not be used for more than a few hours after being compounded and should be made up new at least each day.

PROCEDURE.—Boil the sample for a few minutes in a 0.5% NaOH solution and disintegrate the fibers thoroughly by shaking in a test-tube as previously described. Place a small amount of the fibers on a microscope slide and dry by the use of hardened filter or blotting paper. Then place 2 or 3 drops of the compound stain on the fibers and let them remain 2 minutes. In the meantime tease the fibers apart and move them about in the stain on the slide. This is necessary in order to allow the stain to have equal opportunity to act on all the fibers. At the end of 2 minutes, remove the excess stain with 3 or 4 thicknesses of hardened filter paper and treat the fibers with 3 or 4 drops of a very dilute HCl solution (1:1000). Let the acid solution remain on the slide for 10–30 seconds while the fibers are being teased apart and moved about rapidly; then remove the excess acid solution with filter paper, add 3 or 4 drops of distilled water, quickly tease the fibers about and absorb the water with filter paper. If all the excess stain has been removed from the slide at this point, add a drop or two of water, spread the fibers about on the slide, and place a cover-glass over them. If too much stain remains on the slide at this point, however, it will be necessary to rinse again with distilled water before applying the cover-glass. After the cover-glass has been placed in position the fibers are ready for examination under the microscope.

Distinction between Bleached and Unbleached Chemical Wood Pulp.*—The following method of C. G. Bright will in general give a distinction between pure cellulose fibers and those which contain lignin. Rags, bleached sulfite, and soda or any thoroughly bleached materials are stained *red*, while unbleached sulfite, ground wood, jute, or any lignified materials are stained *blue*. The principal application lies in the estimation of unbleached pulp in book papers. As a cheaper paper can be made by substituting unbleached sulfite, for instance, for bleached sulfite it is often important to know how much unbleached pulp there is in a paper.

* "Paper Testing Methods," Tappi Publishing Co., (1922).

SOLUTIONS.—(*A*) *0.1 N Ferric Chloride:* Dissolve 2.7 grams of $FeCl_3 \cdot 6H_2O$ in water and dilute to 100 cc.

(*B*) *0.1 N Potassium Ferricyanide:* Dissolve 3.29 grams of $K_3Fe(CN)_6$ and dilute to 100 cc.

(*C*) *Substantive Red:* Dissolve 0.4 gram of benzopurpurin 4B extra (Bayer Co.), and 0.1 gram of oxamine brilliant red BX (Badische Co.) in 100 cc. of hot water. Stir the dyes into the water slowly.

Filter solutions *A* and *B* each through a fresh filter into clear glass-stoppered bottles. Mix equal volumes fresh whenever the reagent is used. Use the staining solutions in tall, narrow, cylindrical beakers set in a water bath. Suspend the slides in a beaker by a clamp which holds them at their upper ends, the clamps resting across the top of the beakers. Heat the bath by a small Bunsen burner with a pilot flame so that when the required temperature is reached the pilot flame may be used to maintain it. Suspend a thermometer in the stain and have the beaker containing the stain as small as possible so as not to use too much stain at one time.

PROCEDURE.—Mix equal volumes of solutions *A* and *B* and heat to 35° C. in the water bath, regulating the pilot flame so that the temperature will remain constant within 1° for a period of not less than 15 minutes. Prepare a suspension of the fibers in water in a test-tube as previously described. The suspension of fibers should be more diluted with water than when preparing for use with the Herzberg stain. Shake the test-tube well, insert a glass dropping tube (a 10-inch glass tube about $\frac{7}{32}$ inch in diameter with a small rubber bulb on one end) as quickly as possible 2 inches below the surface. Expel 2 bubbles of air and draw up a little less than 0.5 inch of the mixture in the tube. Transfer this to the slides, completely emptying the dropper, which will make 4 drops. Place the slides in an air bath to evaporate the moisture. Do not let the dried slides remain in the oven after the water is evaporated. Dip the dry slide in distilled water to moisten it uniformly so that air bubbles will not be formed when it is immersed in the stain. If dipping in water still leaves bubbles, they can be removed by blowing across the slide from the edge. Then suspend the slide in the stain and leave it there for 15 minutes at 35° C. Remove and wash by

dipping in and out of a beaker of water six times and repeating the process in a fresh beaker of water. If the fibers have been loosened to any extent by this treatment, dry out the slide again otherwise it can be placed directly in the red solution *C*.

Heat a portion of solution *C* to 45° C. and suspend the slide in it for 5 minutes at this temperature, after moistening and excluding bubbles as before. Immediately wash the slide in 2 beakers of water, then dry and place a cover-glass on the dry slide with a drop of balsam. The slide is then ready for microscopical examination.

NOTES.—(1) To get the best results distilled water must be used throughout and the staining solutions must be fresh. Solutions *A* and *B* will keep well if placed in separate bottles. Solution *C* should be made freshly each time, as it gets thick and stringy on standing, especially after heating.

(2) Unbleached sulfite from different mills varies considerably in lignin content, therefore some stains a deeper blue than others. With pulp containing more lignin it is possible to use a little stronger treatment with the red, which gives a better color on the bleached without affecting the unbleached.

(3) It is very necessary to wash out or neutralize all alkali in the fibers, as the blue is decolorized by alkali.

Qualitative Test for Ground Wood.—There are several reagents which, when applied to the surface of a paper, show characteristic colors if ground wood is present. Such tests, however, are of questionable value in arriving at any estimation of the amount of ground wood and microscopical examinations should always be made. The principal test solutions for the presence of ground wood are as follows:

(1) *Aniline Sulfate.*—Dissolve 5 grams of aniline sulfate in 50 cc. of distilled water and add a drop of conc. H_2SO_4. This solution is not permanent, but decomposes rather easily, taking on a violet coloration. It should be used only when it is colorless. When applied to paper containing ground wood, it gives a bright yellow color.

(2) *Phloroglucinol.*—Either one of the following formulas may be used:

Formula 1.—Dissolve 1 gram of phloroglucinol in 50 cc. of alcohol and add about 25 cc. of conc. HCl.

Formula 2.—Dissolve 1 gram of phloroglucinol in 25 cc. of water and add 25 cc. of conc. HCl.

These solutions keep fairly well when protected from air and light. A fresh solution works more sharply and quickly than an old one. The color which it gives on paper containing ground wood is a bright magenta.

(CAUTION.—Jute, manila, and unbleached sulfite sometimes give a pale pink coloration. An indication of traces of ground wood by this test should therefore be confirmed by a microscopical examination.)

(3) *Dimethyl-p-phenylenediamine* (*Würster's Reagent*).—A water solution of this compound, when dropped upon a paper containing ground wood, gives an orange-red spot after a short interval.

(4) *Nitric Acid.*—Conc. HNO_3 when applied to a paper containing ground wood gives a deep yellow color.

STANDARD PAPERS FOR FIBER ANALYSIS

General.—Before making up any standard papers, the raw materials should be tested to see that they are pure sulfite, soda, rag, etc.

Sulfite-rag Standards.—Pure sulfite pulp and unfilled pure rag paper should be used for the sulfite-rag standards. After determining the moisture in each, weigh them out into 100-gram bundles and place in a tightly covered can. When it is desired to make up a certain sulfite-rag standard, the amount of bone-dry stock required should be calculated from the moisture figures, the 100-gram bundles reweighed, and correction made for any change in moisture content which may take place during storage. The proper weight of the stock having been determined, add the sulfite to the beater and partly cut down; then add the rag paper and beat the two for some time, with the knives down. Raise the knives and stir the contents of the beater for $1\frac{1}{2}$–2 hours. Make up sheets from this stock on a hand mold, press between blotters, and mark for identification.

Soda-rag Standards.—Follow the same procedure as for the sulfite-rag standards, using, however, pure soda pulp in place of sulfite pulp.

Other Standards.—For other standard papers follow the same general procedure, taking special precaution to make certain of the purity of the original raw materials.

CHEMICAL ANALYSIS OF PAPER

General.—The analyses described in this method do not include fiber analysis, which is described on page 445. For the determination of tarnishing properties and for sizing tests see pages 480 and 476, respectively.

Mineral Matter (Ash).—Ignite 2 grams in a porcelain crucible until all the carbon has been burned off, brush the ash carefully into a balanced watch glass and weigh it. Since the ash of paper is generally very light, great care must be taken that none of it is blown out of the crucible by drafts of air. For this reason the crucible should always be kept covered after the main portion of the organic matter has been burned off and the paper should not be allowed to take fire and burn.

NOTES.—(1) If the paper is filled with crown filler, moisten the ash with a little dil. H_2SO_4 to convert any CaS to $CaSO_4$; then evaporate to dryness and ignite strongly. Multiply the ash as actually determined by 1.265 to obtain the equivalent of $CaSO_4 \cdot 2H_2O$ as it existed in the sheet.

(2) Unfilled papers sometimes show a blue ash, due to the presence of ultramarine. The amount of the latter may be determined in many cases by carefully igniting a considerable quantity of the paper until all the carbon has been burned off, then taking a quantity of clay or calcium sulfate equal to the weight of the ash and determining how much of a standard sample of ultramarine must be mixed with this to produce the depth of color shown by the ash.

Filler.—As a rule, the presence of more than 2% of ash in a white paper indicates that it contains added filler or loading material.* It should be borne in mind, however, that the ash itself will not indicate the actual amount of filler in the paper since the filler always contains more or less moisture and volatile matter which is driven off when the paper is ashed. The nature of the filler will be indicated by qualitative tests as follows:

Boil the ash with dil. HCl, filter on a quantitative filter and wash. Test a portion of the filtrate for sulfates by boiling with a small amount of $BaCl_2$ solution. Test the remainder of the filtrate for Al by adding an excess of NH_4OH. Then filter and test the filtrate for Ca by adding $(NH_4)_2C_2O_4$. The presence of

* A paper may show an ash as high as 3–5% without being loaded, due to the ash of the pulp and mineral matter derived from water, alum, and sizing materials.

any considerable amount of Ca and of sulfate at this point indicates that the paper is filled with crown filler, $CaSO_4 \cdot 2H_2O$; whereas only a small amount of Ca would probably be due to lime in clay or other insoluble filler.

Transfer the residue insoluble in HCl to a platinum crucible, burn off the filter paper, and then fuse with Na_2CO_3 to a clear fusion. Digest the fusion with hot water until it can be removed from the crucible. Dissolve a small portion of the residue insoluble in hot water in dilute HCl; if it gives a clear solution, this indicates the absence of $BaSO_4$. In this case dissolve the entire fusion in HCl and evaporate to dryness. Take up with warm, dil. HCl and filter. The insoluble residue will be SiO_2.

In case the original fusion does not dissolve in HCl, boil it with water, filter and wash thoroughly. Dissolve the residue insoluble in hot water in dil. HCl and add dil. H_2SO_4. A white precipitate shows the presence of Ba. Acidify a portion of the water solution with HCl and add $BaCl_2$ solution. A white precipitate shows the presence of sulfates.

To the bulk of the HCl solution of the fusion, or to the bulk of the water solution (after adding an excess of HCl and boiling) add a slight excess of NH_4OH and boil. A white gelatinous precipitate shows Al. Filter, and to the filtrate add an excess of $(NH_4)_2C_2O_4$ solution. A white precipitate shows the presence of Ca. Filter, acidify the filtrate with HCl, and evaporate to the point of crystallization. Cool, and add an excess of ammonia and Na-phosphate solution. Stir thoroughly. A white crystalline precipitate shows the presence of Mg.

Interpretation of Results.—A considerable amount of CaO and sulfate soluble in HCl indicates crown filler, $CaSO_4 \cdot 2H_2O$. The presence of Ba and of SO_3 in the insoluble residue indicates blanc fixe, $BaSO_4$. The presence of Ba soluble in HCl with effervescence indicates $BaCO_3$. An alkaline ash showing lime soluble in HCl, but not showing SO_3, indicates $CaCO_3$ (whiting or chalk). Considerable amounts of SiO_2 and Al, with or without small amounts of Ca and Mg, indicate china clay; but if the amount of Mg is considerable, the filler is probably agalite, talc, or asbestine. A microscopical examination of the ash will often give a clue as to the nature of the filler. Agalite crystallizes in needles; asbestine is fibrous.

NOTE.—It is not usually possible to distinguish between talc and clay containing a little MgO without a quantitative determination of the amount of MgO in the ash of the paper. It is sufficiently accurate to treat the ash in a platinum crucible with H_2SO_4 and evaporate once or twice with HF to remove SiO_2. Then take up the residue in warm dil. HCl (it should practically all dissolve unless Ba salts are present), add NH_4OH, boil until the odor of NH_3 is nearly gone and then add, without filtering, a slight excess of $(NH_4)_2C_2O_4$. Filter, wash with hot water, add a slight excess of HCl and evaporate till crystallization begins. Dilute until the crystals just dissolve and precipitate the Mg as $MgNH_4PO_4$ in the usual way. Ignite and weigh as $Mg_2P_2O_7$ and calculate the percentage of MgO in the weight of paper ash taken. Clay rarely contains over a few per cent of MgO, whereas talc contains approximately 31%.

Retention.—The retention is generally calculated from the ash, although for accurate results, the ash should be corrected for the natural moisture in the filler. The calculation of retention is as follows:

Subtract the percentage of filler from 100% to obtain the percentage of fiber in the sheet; divide the pounds of fiber furnished by the percentage of fiber in the paper to obtain the pounds of paper made from the engine. From this figure subtract the pounds of fiber furnished and the balance is the pounds of filler retained. This figure, divided by the pounds of filler furnished and multiplied by 100, gives the percentage of retention.

Acidity.—Papers containing free acid are rare. For practical purposes, however, the acidity due to excess of alum is to be considered free acid.

TOTAL ACIDITY.—For purposes of comparison, total acidity may be determined as follows:

Warm 5 grams of paper with 250 cc. of distilled water, pour off the water and titrate while still hot with 0.1 N NaOH and phenolphthalein until a permanent pink color is obtained. Run a blank on an equal amount of the water. Subtract the blank titration from the other titration and calculate the difference to SO_3, or if desired, to alum.

CALCULATION.—1 cc. 0.1 N NaOH = 0.004 gram SO_3.
= 0.011 gram $Al_2(SO_4)_3 \cdot 18H_2O$.

SULFUROUS ACID.—Tear up 50 grams of the paper and place in a 500-cc. distilling flask with about 350 cc. of distilled water. Distill until 150 cc. have come over and collect the distillate in a

flask containing about 50 cc. of water with a few drops of bromine water added to it. Acidify with dil. HCl and boil off the Br; then add a slight excess of $BaCl_2$ solution. Boil till the precipitate settles clear. Filter out the $BaSO_4$, ignite, and weigh in the usual manner. From the weight of $BaSO_4$, calculate the amount of SO_2.

CALCULATION.—$BaSO_4 \times 0.2744 = SO_2$.

NOTE.—Qualitative tests for the acidity of the paper are generally sufficient. A satisfactory paper should not give more than a slight acid reaction when pressed in contact with moistened blue litmus paper between sheets of filter paper for 15 minutes. Sulfurous acid in papers that have been exposed to the air for any length of time is oxidized to sulfuric acid.

Free Chlorine.—Free Cl is seldom found in papers. If present, it can be detected by placing the paper in a dilute solution of KI made weakly acid with H_2SO_4, to which has also been added a few drops of starch solution. Free Cl in the paper will liberate iodine, which will give a blue color with the starch. If desired, the amount can be determined by titrating the iodine with 0.1 N thiosulfate solution.

Chlorides.—Free chlorine or hypochlorites from excess of bleach in the paper do not remain as such for any length of time but are reduced to chlorides. The presence of the latter, however, in appreciable amount is also objectionable. To determine the amount of chlorides present, weigh 5–10 grams of the paper, tear it up in small bits and heat to boiling with water in a beaker. Pour off the water and repeat the boiling with 2 fresh portions of water. Filter the combined extracts if necessary. Add a few drops of dil. HNO_3 and a slight excess of $AgNO_3$ solution. Filter the AgCl on a Gooch crucible. Wash with hot water, dry and weigh. Calculate to Cl.

CALCULATION.—$AgCl \times 0.2474 = Cl$.

NOTE.—If preferred, the solution may be titrated with 0.1 N or 0.02 N $AgNO_3$, using K_2CrO_4 solution as an indicator. (See p. 687.)

COATED PAPERS

The coating consists of a mineral substance or substances with an adhesive binder to make a coherent film upon the surface of the paper. When papers are properly coated, the coating should

not "pick" or lift off when the moistened thumb is pressed momentarily against the coating and then withdrawn with a quick jerk. In the case of poorly coated papers, more or less of the coating will adhere to the thumb when thus tested. Papers may be single coated (coated on one side) or double coated (coated on both sides).

Amount of Coating.—Weigh a piece of the paper cut to exact dimensions (2×5 inches is usually a convenient size) and place in a flat glass dish. The dishes used for developing in photography are convenient for this purpose. Cover with water containing 1% of NH_4OH and set aside in a warm place (2 or 3 hours is generally sufficient to loosen the coating). Remove the paper to a large watch glass, rub the surface with a small camel's-hair brush cut off square, and wash the coating into a beaker. If the paper is double coated, turn it over and repeat on the other side. Continue the operation until all the coating is washed into the beaker. Dry the paper and weigh it under the same conditions as those under which the original paper was weighed. The loss in weight is the weight of coating. Calculate this to percentage of the original sample and also figure the weight of coating on the basis of a ream of 500 sheets 24×40 inches (see Table XXI, p. 469).

Analysis of Coating.—Heat the mixture in the beaker to boiling and filter through a qualitative filter. Test the filtrate for glue, casein, and starch. For the qualitative tests for glue and starch, see page 476. Casein can generally be detected by the odor and also by the fact that it will precipitate from the solution when carefully neutralized with HCl. A confirmatory test for casein may be made on the original paper as follows:

Boil 1 or 2 square inches of the paper with 5 cc. of water containing about 5 drops of dil. H_2SO_4. Decant the liquid from the paper into a test-tube, cool and add 1 drop (not more) of 3% formaldehyde. Mix and pour this solution gently down the side of an inclined test-tube containing 2 cc. of conc. H_2SO_4 to which has been added 1 drop only of 10% $FeCl_3$ solution, taking care that the water solution flows on the top of the H_2SO_4 without mixing with it. If casein is present, a violet ring forms at the junction of the liquids. Glue does not give more than a brownish color and rosin does not react. A blank test should be conducted.

using a small amount of casein, or preferably, a paper which is known to contain casein.

The usual substances to be looked for in the mineral part of the coating are (1) blanc fixe, $BaSO_4$; (2) satin white, a mixture of $CaSO_4 \cdot 2H_2O$, $Ca(OH)_2$ and $Al(OH)_3$; (3) china clay, aluminum silicate (approximately $Al_2Si_2O_7 \cdot H_2O$); and (4) chalk or whiting, $CaCO_3$.

Wash the residue on the filter paper into a beaker with a stream of water, first punching a hole in the paper. Pour 10–15 cc. of hot dil. HCl through the filter into the same beaker. Heat the solution to boiling (note whether the acid causes effervescence of CO_2). Let settle, decant through a quantitative filter, and heat the residue in the beaker with a second portion of 100 cc. of dil. HCl. Filter through the same filter, washing with hot water. Divide the filtrate into 2 portions. Test one for sulfates with $BaCl_2$ solution and the other for Al and Ca. The presence of Ca, Al and SO_4 indicates that satin white was used in the coating. If Ca is found but no SO_4 and if the coating gives an effervescence with HCl, it contains chalk or whiting ($CaCO_3$). If the coating contains carbonates but is free from Ca (and Mg), test the HCl solution for Ba, as in some special papers $BaCO_3$ is used.

Ignite the filter containing the residue from the HCl treatment above, and fuse with excess of Na_2CO_3 in a platinum crucible. Boil the fusion with water and filter, washing well with hot water. To the filtrate add HCl in excess and boil off all CO_2. Test a portion of the solution for sulfate with $BaCl_2$ solution. Evaporate the remainder to dryness, take up with HCl and note whether any SiO_2 is present. If so, filter out and test the filtrate for Al_2O_3 by boiling with an excess of NH_4OH. A slight precipitate here may be due to alum from the paper; a heavy precipitate indicates china clay, if silica was also found present. Add $(NH_4)_2C_2O_4$ solution to the filtrate from the alumina, boil and filter out any CaC_2O_4 that may precipitate. Test this filtrate for Mg, which in considerable amount might indicate the presence of talc.

Dissolve the water-insoluble portion of the fusion with HCl. Test a portion of it for Ba with H_2SO_4. If a precipitate is obtained, confirm this by dipping a platinum wire into the remainder of the HCl solution and holding it in the flame. Ba will give a green coloration to the flame. If both Ba and sulfate

are found in the fusion of the residue insoluble in HCl, the coating contains blanc fixe.

NOTE.—After removing the coating, the uncoated paper may be tested for ash and filler as previously described. The test for rosin, if called for, should be made on the original paper.

Waxed Papers

Paraffin.—Cut 2–5 grams of the paper into strips and fold in numerous small crosswise folds as in the determination of Rosin (p. 478). Cover with CCl_4 in a Soxhlet extractor and extract until the paraffin is all removed, collecting the extract in a weighed flask. Evaporate off the solvent (which may be recovered for subsequent use), dry the extract at 105° C., cool in a desiccator and weigh. Express results as percentage of the waxed paper and as pounds of paraffin per ream of the *extracted* paper.

REFERENCES.—Herzberg: "Papier-prüfung"; Griffin and Little: "The Chemistry of Paper Making"; *U. S. Dept. Agr., Report* No. 89, by F. P. Veitch; Methods of the Technical Association of Pulp and Paper Industry.

PHYSICAL TESTING OF PAPER

General.—Before cutting the samples for the physical tests, it is necessary to determine the machine and cross directions of the sheet. Depending on the individual papers, one of the following methods may be used:

(*a*) Cut a circle 1 or 2 inches in diameter from the sheet and moisten on one side. The paper will curl about an axis corresponding to the machine direction of the paper.

(*b*) Cut a strip $\frac{1}{2}$ inch wide and 6–8 inches long from each direction of the sheet, hold the ends together and let the strips bend of their own weight, first to the right and then to the left. The paper is less flexible in the machine direction, hence when the machine direction is uppermost there will be an opening between it and the lower strip. When bent the other way, the two strips will lie together and the cross-direction strip will then be on top.

(*c*) The direction can sometimes be told, especially on cylinder-made papers, by examining the surface of the sheet. The fibers will have a very marked tendency to be drawn out along one direction, namely the machine direction.

(*d*) Certain papers tear straight in the machine direction and very unevenly in the opposite direction.

(*e*) The form of break made by the Mullen tester also shows the machine direction. The longest or chief line of rupture is always *across* the machine direction.

(*f*) The tensile strength of strips cut in the machine direction is generally greater than of those cut in the cross direction, the ratio usually being nearly 2:1.

NOTE.—Envelopes are generally folded so that the machine and cross directions of the paper run diagonally on the face of the envelope.

Effect of Humidity.—Humidity has a marked effect on the physical characteristics of paper. The folding test is most affected and the bursting strength least affected by humidity changes. The breaking strength and tearing resistance fall in between these extremes. In general it has been found by the Bureau of Standards* that the different tests are affected as follows: The moisture content, ream weight, and thickness increase at varying rates with increase in relative humidity. Tensile strength and bursting strength increase up to the range of 35–40% relative humidity and decrease above this range. The amount of change depends upon the kind of paper and the relative change is practically the same for the machine and cross directions. Elongation increases continuously with the moisture content. The tearing strength also increases with relative humidity, the extent depending upon the kind of paper. The folding endurance increases with humidity, but there is a very marked variation from one grade of paper to another and little concordance of results in the machine and cross directions.

For purposes of record, the relative humidity and the temperature should always be recorded at the time the tests are made and it is preferable to conduct the tests in a room where temperature and humidity are maintained constant. A relative humidity of 65–70% at about 65° F. is recommended as standard.

Tensile Strength.—Make the determination on the Schopper tensile machine (Fig. 22). Cut strips from both directions of the paper exactly 15 mm. wide and about 240 mm. long, if it is

* "The Effect of Atmospheric Humidity in the Physical Testing of Paper"; *Tech. Assoc. Papers*, series 6, 64 (June, 1923).

possible to obtain strips of this length *without folds*. A strip of this length can be used where the jaws are 180 mm. apart, in which case the percentage stretch can be read directly from the scale. Test at least 5 strips cut from each direction and report the average of the 5 tests. If the individual tests vary consider-

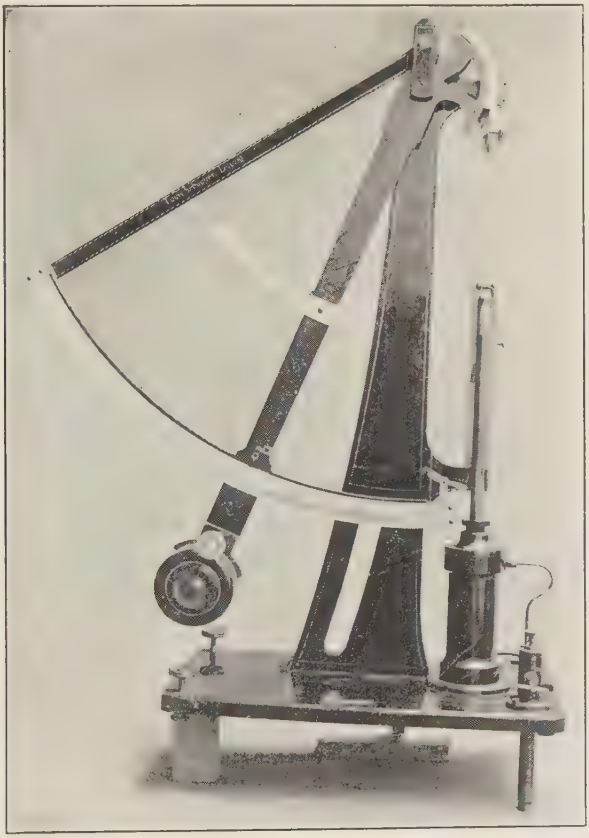


Fig. 22.—Schopper Tensile Machine.

ably, run at least 10 in each direction. Disregard any tests where the strip breaks at, or in, the jaw. In placing the strip in the machine, first clamp it in the lower jaw, at right angles to the jaw, then pull it through the upper jaw and clamp. Adjust the stretch device catch and release the locks on the upper jaw and on

the pendulum previous to starting the machine. Results are obtained in kilograms per 15 mm. Calculate to pounds per inch.

CALCULATION.—Kg. per 15 mm. $\times 3.73 =$ lbs. per inch.

Breaking Length.—The breaking length is the length of a paper strip which, if suspended at one end, would just break of its own weight. For the calculation of breaking length, weigh all the strips together previous to testing and also determine the total length of the strips in millimeters. Calculate as follows:

Breaking length (yards) =

$$\frac{\text{Tensile strength (kilograms per 15 mm.)} \times \text{Total length (mm.)} \times 1.094}{\text{Total weight (grams)}}$$

If the ream weight ($25 \times 40 - 500$) is known, the following formula may be used:

$$\text{Breaking length} = \frac{\text{Tensile strength (kilograms per 15 mm.)} \times 51{,}850}{\text{Ream weight}}$$

The breaking length usually ranges from an upper extreme of 11,000 yards for strong kraft paper down to about 2000 yards for a weak paper.

Breaking Factor.—The breaking factor or tensile factor is the tensile strength (pounds per inch) in each direction, divided by the weight in pounds of a ream of 500 sheets, 25×40 inches.

Wet Tensile Test.—The wet tensile test is of particular value in testing blueprint papers. Cut strips as described above and immerse them in water at 70° F. for 20 minutes immediately before testing. The conditions must be strictly observed as both the temperature of the water and the time of soaking materially influence the results. Especial care must be taken in fitting the strips into the jaws of the machine and having the strips in accurate alignment so that no tearing effect is produced.

Stretch Test.—If a 180-mm. strip is used for testing, the stretch will be given directly by the machine, in percentage. If a shorter strip is used, the percentage stretch will have to be calculated from the actual stretch in millimeters.

Folding Test.—Determine the folding strength in double folds on the Schopper folding machine (Fig. 23). Cut the strips for testing 15 mm. wide and about $\frac{1}{8}$ inch longer than the strip gage accompanying the folding machine. Fasten the strip in the jaws after releasing the tension of the jaw heads. After the

strip is in place, pull back the jaw heads, set the gage at zero and release the lock on the wheel. The machine should run at 120 r.p.m. Test at least 5 strips in each direction. (Test 10 if the individual results vary widely.)

The folding result is very much affected by the relative humidity of the atmosphere.

The *folding factor* is the folding strength in each direction divided by the weight in pounds of a ream of 500 sheets, 25×40 inches.

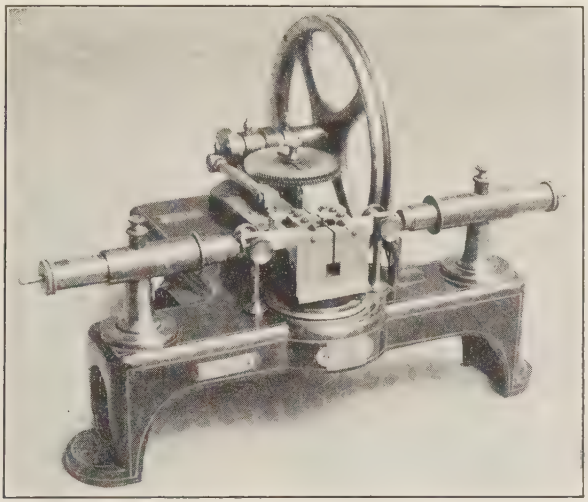


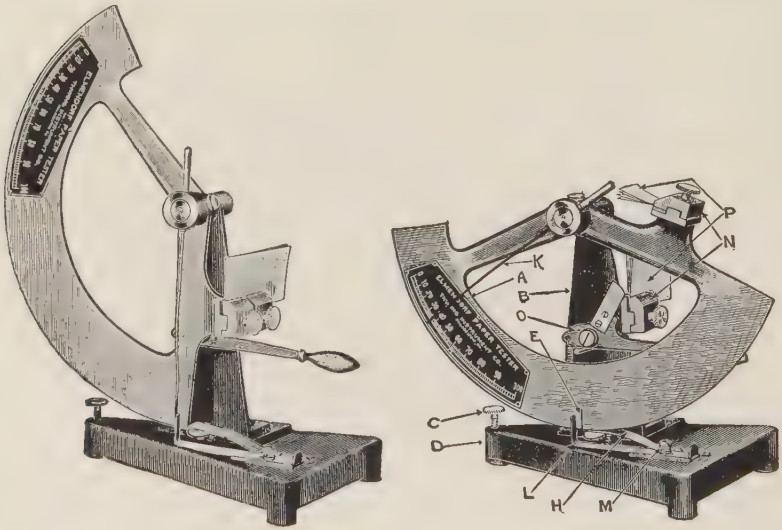
Fig. 23.—Schopper Folding Machine.

Note.—It is very necessary that the small steel wheels which support the clamping jaws be perfectly round, well oiled, and revolve easily as the jaws move back and forth, as otherwise results may be seriously affected.

Tearing Test (Elmendorf).—Determine the tearing strength on the Elmendorf tearing tester* (Fig. 24). This consists essentially of a heavy pendulum mounted on ball bearings. The sector *A* carries a clamp *N* and a dial graduated from 0 to 100. On the same axis a pointer is mounted which has a constant friction just sufficient to stop at the highest point reached by the swing of the sector.

* Manufactured by the Thwing Instrument Co., 3339 Lancaster Ave., Philadelphia, Pa.

Before making the tests, level the instrument with the leveling screw C in the base D so that the white mark E on the sector is opposite the end of the spring stop H, when the latter is depressed and the sector is free to swing. Test for zero by pushing the sector to the left until the spring stop engages the right-hand edge of the sector. Set the pointer K against the pointer stop L which is fastened to the base by a screw M. Release the sector by depressing the spring stop as far as it will go and hold it down until the sector has swung once in each direction. Release



At start of test At finish of test

FIG. 24.—Elmendorf Tearing Tester.

the spring stop to damp the swing of the sector and note the reading of the pointer. If not at zero, adjust the position of the pointer stop by means of the screw M until the pointer on further trial comes to zero. It is very important that the instrument be set at the proper zero, as the accuracy of the test is the same as the accuracy of the zero. While no further adjusting is usually required, it is well to make a test for zero at intervals.

Cut several pieces from each direction of the paper with their edges against the gage of the paper cutter which comes with the tester. Set the sector and the pointer as in the zero test. Open

both jaws of the paper clamps *N* and insert 2, 4, 8, or 16 sheets, seeing that all sheets touch the bottom of the jaws. The sheets should reach about 1 inch into the movable jaw, leaving the longer portion to be used for repeat tests. Clamp both jaws tight, depress the cutter lever *O* to low position and release. Then depress the spring stop as far as it will go and hold it down until the sector has swung once in each direction. The sector will swing a distance indicated by the position of the pointer. If 8 sheets are used, multiply the reading by 2 to express the tearing strength in grams; if 4 sheets, multiply by 4; and if 2 sheets, multiply by 8. The best accuracy will be obtained if readings lie between 20 and 40. If readings are above 60, too many sheets are being used. Make 5 separate tests in each direction of the paper and report the average figure.

NOTE.—If the instrument has been idle for some time, the plunger or pin which engages in the groove of the pointer hub may become gummed up and stick. To clean this the pointer should be pulled off of the hub on which it rides and the pin which slides in the hub groove should be wiped off and a drop of clock oil put on it so the pin will not stick, but will move freely up and down in the stem guide. It is not necessary to put any oil on the pointer hub, but it should be wiped off well.

Mullen Test (Bursting Strength) and Thickness.—Use the small Mullen machine (Fig. 25) for light-weight papers and the large (Jumbo) machine for heavier-weight papers and cardboard. Make at least 5 tests (preferably 10)* and report the average. The reading of the gage is in pounds per square inch. The gage used should be such that the bursting strength of the paper does not come within 25% of either end of the scale readings. It should be frequently calibrated.

Place the sheet over the diaphragm and clamp securely. Make sure that the sheet is smooth and that no wrinkles or creases occur within the space to be tested. Set the pressure gage at zero and apply pressure by turning the wheel with a

* The National Association of Corrugated Fiber Box Manufacturers requires that 3 tests be made on each side of a square-foot sample of container board. It is well in testing material made up from several plies, or where both sides are not the same, to make an equal number of tests on each side.

smooth, rapid motion free from jerks.* When the paper breaks, immediately reverse the wheel to remove pressure on the diaphragm and then take the reading of the gage.

Measure the thickness by a number of tests, using a thickness gage (Fig 26), and taking the test near each Mullen break. Average the Mullen tests and thickness results. The average Mullen test, divided by the thickness in ten thousandths of an inch, is the *strength ratio*, or *bursting ratio.*

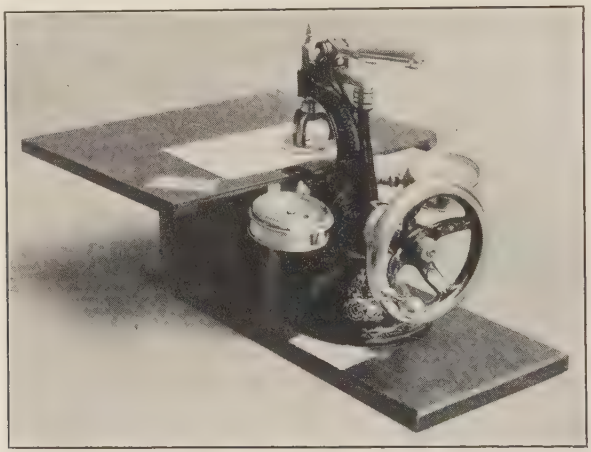


Fig. 25.—Perkins Mullen Tester.

Example.—Mullen test = 20 pounds, and thickness = 0.0018 inch. Then the strength ratio = $20 \div 18 = 1.11$.

The average Mullen strength divided by the weight in pounds of a ream of 500 sheets, 25×40 inches, is the *strength factor* or the *bursting factor.*

Note.—In the case of kraft papers the strength factor is figured on a ream of 480 sheets, 24×36 inches. On this basis a No. 1 quality kraft should show a strength factor of 1.00 or greater.

Brittleness Test.—An indication of the relative brittleness of paper may be obtained by creasing the paper between rolls of a definite weight and determining the bursting strength of the

* The manufacturers recommend that the wheel be turned at a constant and uniform speed of about 2 revolutions per second.

paper on the line of the crease. The following procedure is recommended:*

Crease the paper by folding it in the cross direction and running it under a roll weighing approximately 5 pounds. Then fold the paper back on the same crease and again run it under the roll, thus giving it a double crease. Place the paper on the Mullen tester and determine the bursting strength with the creased line in the center of the diaphragm. Make 10 separate tests and take

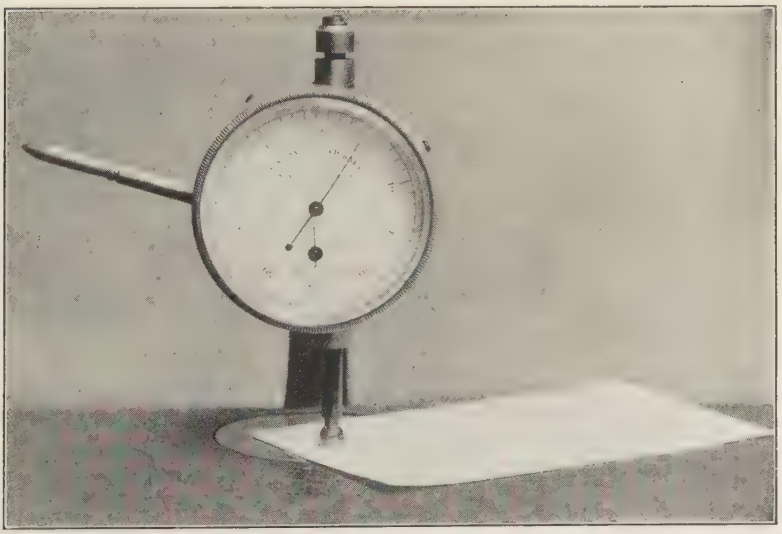


FIG. 26.—Thickness Gage.

the average. Figure the percentage loss of the bursting strength of the creased paper as compared with its original bursting strength. The term Pop Fold has been proposed for the result thus obtained and the figure is a measure of the relative brittleness of the paper.

Ream Weight.—If a sufficiently large sample of the paper is available, weigh a sheet of the desired size on the ream-weight scales (Fig. 27),† which give directly the weight of a ream of 500 sheets or 480 sheets, as the case may be. For instance, if the

* See article by P. L. Houston of the U. S. Bur. of Standards published in *Tech. Assoc. Papers*, series 6, 117 (June, 1923).

† There are also several other types of ream-weight scales.

ream weight $24\times36-500$ is desired, one sheet 24×36 inches weighed on the ream-weight scales would give the ream weight in pounds direct. In case the size of the sample is limited, cut a small piece of the paper to accurate measurement, weigh on a precision balance, and calculate the ream weight from this weight. A piece 2×5 inches (*i.e.*, 10 square inches in area) is a convenient size.

The standard commercial ream for writing and printing papers is 500 sheets each 24×36 inches, and unless otherwise specified

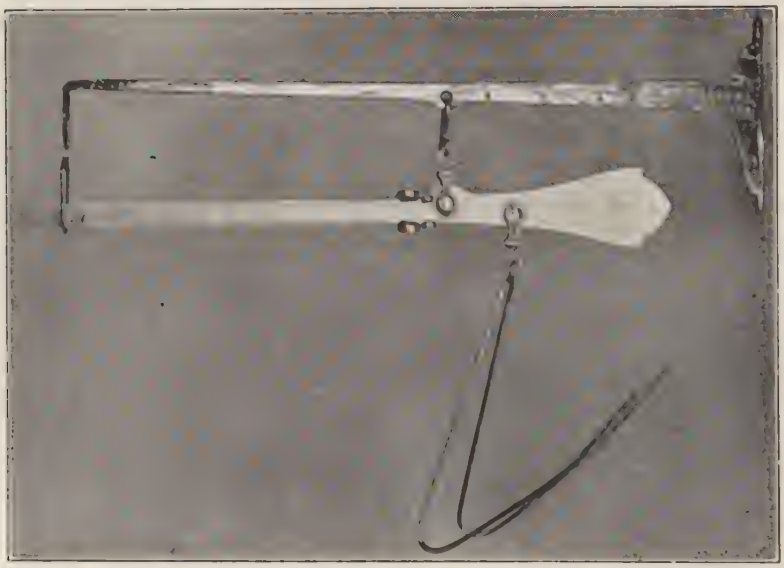


FIG. 27.—Ream Weight Scales. (Fairbanks Co.)

the ream weight should be reported on this basis. If a piece 10 square inches in area is employed, then:

$$\text{Weight in grams}\times95.2=\text{ream weight.}$$

The designation of the size of the ream, etc., is as follows: Ream weight $24\times36-500$, 50 pounds. For wrapping papers and tissues the ream is generally 480 sheets instead of 500 sheets.

For laboratory and test records the standard ream is 500 sheets, 25×40 inches. This is a convenient size for purposes of calculation since the area of the sheet is 1000 square inches.

Table XXI gives the "factors" with their logarithms for calculating the ream weights, on several different bases, from the weight in grams of a piece 2×5 inches.

TABLE XXI—REAM-WEIGHT FACTORS

Size of Sheet, Inches	Sheets in Ream	"Factor"	Logarithm
8½×11	500	10.31	1.0131
12½×16	500	22.05	1.3433
12½×16	480	21.16	1.3255
14 ×17	500	26.24	1.4190
14 ×17	480	25.19	1.4012
16 ×21	500	37.0	1.5686
16 ×21	480	34.6	1.5385
17 ×22	500	41.2	1.6153
17 ×22	480	39.6	1.5975
17 ×26	500	48.7	1.6877
17 ×26	480	46.8	1.6699
17 ×28	500	52.5	1.7199
17 ×28	480	50.4	1.7021
18 ×24	500	47.6	1.6778
18 ×24	480	45.7	1.6600
19 ×24	500	50.3	1.7013
19 ×24	480	48.3	1.6835
20 ×25	500	55.1	1.7413
20 ×25	480	52.9	1.7235
22 ×34	500	82.4	1.9159
24 ×36	500	95.2	1.9786
24 ×36	480	91.4	1.9608
24 ×38	500	100.6	2.0026
24 ×38	480	96.6	1.9848
25 ×38	500	104.7	2 0199
25 ×38	480	100.5	2.0023
25 ×40	500	110.2	2.0422
26 ×29	500	83.1	1.9196
27 ×39	500	116.1	2.0650
27 ×39	480	111.5	2.0472
28 ×34	500	104.9	2.0208
29 ×52	500	166.2	2.2206
30½×41	500	137.8	2.1393
32 ×44	500	155.2	2.1909
34 ×46	500	172.5	2.2368
34 ×46	480	165.6	2.2190
35 ×45½	500	175.5	2.2443
37 ×49	500	199.8	2.3006
38 ×50	500	209.4	2.3210
40 ×48	500	211.7	2.3257
40 ×48	480	203.2	2.3079
41 ×61	500	275.6	2.4403
44 ×64	500	310.3	2.4918

Substance Number.—In October, 1916, the Writing Paper Manufacturers Association adopted the "substance number"

TABLE XXII—ACTUAL WEIGHTS (FIGURED TO 0.5 POUND) OF STANDARD SUBSTANCE NUMBERS* OF PAPER

Size	Substance								
	No. 13	No. 16	No. 20	No. 24	No. 28	No. 32	No. 36	No. 40	No. 44
Inches									
14×17	8.5	10.0	12.5	15.5	18.0	20.5	23.0	25.5	28.0
14×34	16.5	20.5	25.5	30.5	35.5	40.5	46.0	51.0	56.0
15×19	10.0	12.0	15.0	18.5	21.5	24.5	27.5	30.5	33.5
16×21	11.5	14.5	18.0	21.5	25.0	28.5	32.5	36.0	39.5
16×26	14.5	18.0	22.0	26.5	31.0	35.5	40.0	44.5	49.0
16×42	23.5	29.0	36.0	43.0	50.5	57.5	64.5	72.0	79.0
17×22†	13.0	16.0	20.0	24.0	28.0	32.0	36.0	40.0	44.0
17×26	15.5	19.0	23.5	28.5	33.0	38.0	42.5	47.5	52.0
17×28	16.5	20.5	25.5	30.5	35.5	40.5	46.0	51.0	56.0
17×44	26.0	32.0	40.0	48.0	56.0	64.0	72.0	80.0	88.0
17×56	33.0	40.5	51.0	61.0	71.5	81.5	91.5	102.0	112.0
18×23	14.5	17.5	22.0	26.5	31.0	35.5	40.0	44.5	48.5
18×46	29.0	35.5	44.5	53.0	62.0	71.0	79.5	88.5	97.5
19×24	16.0	19.5	24.5	29.5	34.0	39.0	44.0	49.0	53.5
19×26	17.0	21.0	26.5	31.5	37.0	42.5	47.5	53.0	58.0
19×28	18.5	23.0	28.5	34.0	40.0	45.5	51.0	57.0	62.5
19×30	20.0	24.5	30.5	36.5	42.5	49.0	55.0	61.0	67.0
19×48	31.5	39.0	49.0	58.5	68.5	78.0	88.0	97.5	107.5
20×28	19.5	24.0	30.0	36.0	42.0	48.0	54.0	60.0	66.0
20×56	39.0	48.0	60.0	72.0	84.0	96.0	108.0	120.0	132.0
21×32	23.5	29.0	36.0	43.0	50.5	57.5	64.5	72.0	79.0
21×33	24.0	29.5	37.0	44.5	52.0	59.5	66.5	74.0	81.5
22×25½	19.5	24.0	30.0	36.0	42.0	48.0	54.0	60.0	66.0
22×34	26.0	32.0	40.0	48.0	56.0	64.0	72.0	80.0	88.0
23×28	22.5	27.5	34.5	41.5	48.0	55.0	62.0	69.0	76.0
23×31	25.0	30.5	38.0	45.5	53.5	61.0	68.5	76.0	84.0
23×34	27.0	33.5	42.0	50.0	58.5	67.0	75.5	83.5	92.0
23×36	29.0	35.5	44.5	53.0	62.0	71.0	79.5	88.5	97.5
24×36	30.0	37.0	46.0	55.5	64.5	74.0	83.0	92.5	101.5
24×38	31.5	39.0	49.0	58.5	68.5	78.0	88.0	97.5	107.5
24×48	40.0	49.5	61.5	74.0	86.0	98.5	111.0	123.0	135.5
25×40	35.0	43.0	53.5	64.0	75.0	85.5	96.5	107.0	117.5
26×32	29.0	35.5	44.5	53.5	62.5	71.0	80.0	89.0	98.0
26×33	30.0	36.5	46.0	55.0	64.0	73.5	82.5	92.0	101.0
26×34	30.5	38.0	47.5	56.5	66.0	75.5	85.0	94.5	104.0
26×38	34.5	42.5	53.0	63.5	74.0	84.5	95.0	105.5	116.5
27×40	37.5	46.0	58.0	69.5	81.0	92.5	104.0	115.5	127.0
28×34	33.0	40.5	51.0	61.0	71.5	81.5	91.5	102.0	112.0
28×38	37.0	45.5	57.0	68.5	79.5	91.0	102.5	114.0	125.0
28×40	39.0	48.0	60.0	72.0	84.0	96.0	108.0	120.0	132.0
28×42½	41.5	51.0	63.5	76.5	89.0	102.0	114.5	127.5	140.0
30×38	39.5	49.0	61.0	73.0	85.5	97.5	109.5	122.0	134.0
31×53	57.0	70.5	88.0	105.5	123.0	140.5	158.0	175.5	193.5
34×44	52.0	64.0	80.0	96.0	112.0	128.0	144.0	160.0	176.0

* *Paper*, Dec. 6, 1916, p. 17. † Folio size, basis of standard.

system for designating the weights of writing paper. The folio size (17×22 inches) is taken as the basis and the weight of a ream of 500 sheets of folio size is the Substance Number. By specifying the substance number, therefore, the weight of paper desired is definitely established and the weight per ream of any other size, or the substance number of any paper, the ream weight of which is known on some other basis, may be readily ascertained by reference to Table XXII.

NOTE.—The substance number of small samples may be determined directly on the analytical balance. The weight in centigrams of a piece exactly $2\times2\frac{1}{16}$ inches is its substance number.

Penetration or Sizing Tests.—(*a*) FOR WRITING PAPERS.—Float a piece of paper 1 or 2 inches square on the surface of ink, and note the time in minutes until the ink begins to be visible on the upper surface. The time in minutes is taken as a basis for comparing the relative sizing of different papers (see also p. 472).

NOTE.—In order to avoid discrepancies due to the variation in the ink, the latter should be made according to the following formula given by Schluttig and Neuman in "Die Eisengallustiten":

	Grams
Gallotannic acid (dry)	23.4
Gallic acid (crystals)	7.7
Gum arabic	10.0
Hydrochloric acid	2.5*
Ferrous sulfate crystals ($FeSO_4 \cdot 7H_2O$)	30.0
Soluble blue†	2.0
Water to make up to 1 liter.	

Let settle several days and then decant from any sediment. Keep the temperature of the ink constant and use it but once.

(*b*) FOR PAPERS OTHER THAN WRITING PAPER.—For all papers other than writing papers use the so-called Ferrocyanide Test as follows:

Float a piece of paper about 2 inches square on the surface of a 5% solution of $K_4Fe(CN)_6$ and note the time. Then test the upper surface of the piece of paper from time to time by stroking (across the machine direction) with a small camel's-hair brush

* 2.5 grams of actual HCl are equivalent to 5.8 cc. of conc. HCl.

† Any water-soluble basic aniline dye may be used, such as Bavarian blue (S. and J. No. 478), Niagara blue 3B (National Aniline Co.), etc.

moistened with a solution of $FeCl_3$ (5–10%). When the ferrocyanide has soaked up through the paper sufficiently to come in contact with the $FeCl_3$, it will react the moment the latter is applied and give a blue color. The penetration is then considered complete, the time is again noted, and the length of time since the paper was laid upon the surface of the solution is taken as the measure of its resistance to penetration. In stroking the paper with the camel's-hair brush, take care to select a place on the paper which has not previously been wet with the $FeCl_3$ solution. Report the results to the nearest minute, or, if the time is very short, in seconds.

Water Penetration Tests.—The rate at which water will penetrate the surface of a paper may be taken as an index of the degree or extent of sizing or the "waterproofness" of the paper. The following methods are in common use.

(*A*) TRAY METHOD.—The simplicity of this method makes it convenient for use in comparative control tests on materials like chipboard and container-board. Cut a piece of the paper about 6 inches square, designating the four sides in rotation as *A*, *B*, *C* and *D*. Make 2 cuts in each of the sides *A* and *C*, each cut about 1 inch, parallel to, and 1 inch from, the other 2 sides, *B* and *D*, respectively. Bend up the edges *C* and *D* and fasten to them the flaps made by the cuts, using paper clips. This will form a dish or tray of the paper about 4 inches square and 1 inch deep. Pour into it sufficient water to cover the bottom to a depth of about $\frac{1}{4}$ inch and note with a stop watch the time required to strike through to the opposite side. The water should be at a temperature of 15–20° C. Note the time when the first evidences of penetration occur and also when the area showing wet on the underside is about equivalent to a 50-cent piece.

(*B*) GROUND GLASS METHOD.*—Cut specimens about 6 inches square and fold so as to form boxes 2 inches square and 2 inches high, open at the top, the boxes formed by folding being held by convenient fasteners such as paper clips. Place a clean piece of ground glass on a dark surface, such as black paper, with the ground side uppermost. (The ground glass should be washed occasionally with soap and water and kept perfectly free of grease or other discolorations.) Then place the test boxes on the

* *Paper Trade J.*, **79**, 48 (Sept. 4, 1924).

ground glass surface and fill them to within $\frac{1}{2}$ inch of the top with water at 15–20° C. Lift the boxes from the glass at different time intervals and examine the glass for the first appearance of a water film. The successive intervals between the lifting of the same box must not be too short, since some time is required for the moisture film to form and the film thus formed disappears rapidly by evaporation when the box is lifted. In certain kinds of paper, variation in water resistance in any one sample is considerable and on most papers at least 10 tests should be made on each sample.

The above test may be made applicable to heavy boards and samples of paper too small to be made into boxes as follows: Obtain a cylinder about 2 inches in diameter with the wall about $\frac{1}{8}$ inch in thickness, such as a section of pipe or a round 8-ounce bottle cut off near the bottom and the edge ground flat. From the board or paper to be tested cut a disc somewhat larger than the cross-section of the cylinder. Dip the smoothed end of the cylinder in melted paraffin and let it remain for a short time. Remove it quickly, place it on the disc and let it stand until the paraffin has hardened. Set the specimen on the ground-glass surface and pour in about 2 inches of water. If care has been taken to bring the end of the cylinder in contact with the disc of paper or board while the paraffin is hot and fluid, a good joint will result, capable of supporting a considerable column of water and permitting the specimen to be lifted or slid to one side for observation as in the case of the folded boxes.

(*C*) Curl Method.*—Fill a vessel of at least 2-liters capacity with water at 25° C. $\pm$ 1°. (The larger the vessel the easier it is to hold the temperature constant.) Cut the sample in the shape of a right triangle, one leg of which should be about 2 inches long and in the machine direction of the paper, and the other leg about 3 inches long. Make a crease parallel with, and about $\frac{3}{4}$ inch from, the shorter leg, so that one part of the specimen makes an angle with the remainder. Holding the piece in one hand by the point opposite the shorter leg, place it on the surface of the water so that the shorter leg is against one side of the vessel, in which position it will remain steadier than if placed in the center of the vessel. Start a stop watch simultaneously with this

* See *Paper Trade J.* (Apr. 6, 1922 and Oct. 23, 1924).

operation. The piece will curl and the longer dry portion serves as a pointer as it moves across the field of vision. When the curling in the initial direction ceases and the instant it starts to uncurl, stop the stop watch and record the time. Run several tests, each on a different piece, and report the average of the results.

Blotting Paper.—The absorption tests commonly used on blotting paper are as follows:

(*A*) Strip Test.—Cut strips of the paper, in each direction of the sheet, about $\frac{1}{2}$ inch wide and at least $3\frac{1}{2}$ inches long, and make a pencil mark about $\frac{1}{4}$ inch from one end. Then, starting from this mark, make a series of pencil marks at intervals of $\frac{1}{8}$ inch on the paper for a distance of about $2\frac{1}{2}$ inches. Suspend the strips in water at a temperature of 18–20° C. in such a manner that the surface of the water coincides with the first mark. When the strip is first placed in the water, note the time and at the end of 3, 5, and 10 minutes, respectively, ascertain the rise of the water in the paper by means of the marks upon it. Report the results in sixteenths of an inch, *i.e.*, a paper which shows an absorption of 1 inch will be reported as "Absorption, 16." If necessary, a small quantity of ink may be added to the water to aid in determining the exact rise of the liquid. Test several strips of each sample cut from each direction and report the average absorption.

(*B*) Pipette Test.—Suspend a 1-cc. pipette in such a way that the tip is $\frac{1}{2}$ inch from the surface of the sample. Cut the sample 4 inches square and lay it felt side up on a coarse wire screen which is supported by a large beaker. (This is done to prevent as far as possible the blotting paper from caving in at the center where the liquid falls upon it. The felt side of the paper is the side which does not show wire markings.) It is well to use both distilled water and the previously mentioned standard ink (p. 471) at three temperatures of 15, 20, and 25° C. In simply comparing several samples, however, it is usually sufficient to use either distilled water or ink at 20° C.

Fill the pipette with the liquid and at the same time the liquid is released start a stop watch which is held in the other hand. Measure the time in seconds from the time the liquid is released until it is totally absorbed by the paper; also measure the

diameter of the circular spot on the paper immediately at the completion of the time reading.

NOTE.—The Bureau of Standards* recommends the pipette test as more nearly representing the conditions of use, but the strip test is widely employed.

Greaseproof Paper.—True parchment paper consists of unsized rag paper which has been passed through dil. H_2SO_4. This transforms the surface fibers into a tough gelatinous mass which forms a protective coating for the rest. The process increases the tensile strength from three to four times. Imitation parchments may consist of sulfite or a mixture of sulfite and straw prepared by long beating to give the required degree of translucency. Pergamyn is a greaseproof imitation parchment prepared by treating sulfite with glycerin and an unusually large amount of size.

The so-called Turpentine Test has been used largely in the past for determining whether or not a paper is greaseproof. Owing, however, to the introduction of cheaper grades of so-called greaseproof papers, this test is not always satisfactory because of too rapid evaporation of the turpentine and too rapid penetration. Such papers are more readily distinguished by the Oleic Acid or Red Oil Test.

(*A*) TURPENTINE TEST.—Place a drop or two of turpentine on the paper (free from any creases) and lay it upon a clean white blotting paper. Rub the turpentine with the finger and note how long it takes for it to go through and stain the blotting paper. Strictly greaseproof papers will not show penetration by this test, even after several minutes.

(*B*) OLEIC ACID TEST.—Place a piece of the paper, free from grease or thin spots, on a white blotting paper or filter paper and then place on it a piece of metal tube about $\frac{1}{2}$ inch in diameter (the metal screw-top of a polariscope tube is convenient for this). Place a drop of oleic acid on the paper in the area covered by the ring of the tube. Slide the paper back from the filter or blotting paper at 5-minute intervals, without removing the top, and examine the underlying absorbent paper for first traces of penetration of the oil and then for complete penetration. The lowest grades of imitation parchment or greaseproof paper should not

* *J. Ind. Eng. Chem.* (January, 1918).

show any trace of penetration from the oil in less than 10 minutes, nor complete penetration in less than 20 minutes.

It is advisable to make a fiber examination of the paper in connection with the oleic acid test. True greaseproof papers show the fibers thin and considerably shredded.

NOTE.—The so-called Blister Test which has been considerably used in the past is not reliable. This test consists in holding the paper above a lighted match and noting whether any blisters form on the surface. A greaseproof paper is supposed to blister by this test.

SIZING IN PAPER

General.—Blotting paper and so-called "water-leaf paper" are unsized and rapidly absorb ink or any other liquid by capillary attraction. Papers which are to be used for writing or printing purposes must be sized with some material which will prevent this capillary absorption. Rosin and glue ("animal size") are most commonly used. Starch is also used to some extent, generally together with rosin and glue, particularly in the case of blueprint papers. Paper containing a considerable proportion of rags sometimes contains a small amount of starch due to its incomplete removal from the rags.

It is advisable to make qualitative tests before proceeding with quantitative determinations.

Qualitative Tests.—(*A*) TANNIC ACID TEST FOR GLUE AND CASEIN.—Boil several grams of the paper with water until the volume of the latter is only a few cc. (As soon as the water has come to boiling, a portion of it may be poured off and saved for the starch test.) Filter and cool thoroughly. To this solution add about an equal volume of a cold 10% NaCl solution nearly saturated with tannic acid and freshly filtered. A pale grayish yellow, flocculent precipitate indicates the presence of glue or casein or both (see note 2).

NOTES.—(1) If the paper has been treated with formaldehyde in addition to glue, the latter will be rendered more or less insoluble in hot water. In this case boil the sample with dil. NaOH solution, pour off the solution and make slightly acid with HCl. Cool, and test this solution with tannic acid. Run a blank test with the NaOH to make sure that it contains nothing which will precipitate tannin after acidification.

(2) In case the paper contains starch and gives a precipitate by the above test, the precipitate may be due to the starch. In this case, repeat

the test and, before adding the tannic acid solution, add sufficient HCl to the concentrated water extract of the paper to give about a 2% solution. Digest on the steam bath until the starch is all converted to dextrose and a drop of the solution gives no blue color when added to 5 cc. of very dilute (about 0.001 N) iodine solution. Then cool the solution and add the tannic acid-NaCl solution.

(*B*) Molybdate Test for Glue or Casein.—To the cool water-extract of the paper add half its volume of *neutral* ammonium molybdate solution followed by a few drops of HNO_3. The formation of a white amorphous precipitate shows the presence of glue or casein.

Notes.—(1) The precipitate is soluble to a considerable extent in a strongly acid solution. The usual ammonium molybdate solution used in the laboratory for phosphorus analysis is therefore not suitable for this test as it contains excessive acid.

(2) Instead of using the neutral ammonium molybdate solution followed by a few drops of HNO_3, the following solution may be used: Dissolve 3 grams of ammonium molybdate in 250 cc. of water, then add 25 cc. of dil. HNO_3 (1:3). This reagent is not permanent and on standing for some time will gradually settle out. Add about 1 volume of the reagent to 2 volumes of the cold aqueous extract of the paper.

(3) The molybdate test is very delicate and, in using a $\frac{1}{2}$-gram sample of the paper, if no precipitate is obtained, or even in the case of a slight turbidity, it is reasonably certain that the paper has not been tub-sized with glue.

(4) Starch does not interfere with this test if directions are carefully followed.

(*C*) Rosin (Liebermann-Storch Test).—Place several small pieces (representing about 1–2 grams) of the paper in a clean, *dry* test-tube. Cover with pure acetic anhydride and boil down to about 1 cc. The anhydride fumes are extremely irritating and after they begin to come off from the test-tube it is well to hold the mouth of the latter near a flame so that the fumes will burn as fast as they are driven off. Pour the liquid residue into a clean, *dry* test-tube and cool *thoroughly*. If any waxy particles separate, they should be filtered off. Let 1 drop of conc. H_2SO_4 run carefully down the side of the test-tube. A fugitive rose-violet coloration, formed when the acid meets the anhydride, indicates rosin.

(*D*) Starch.—Boil a portion of the paper with water. Cool and filter if necessary. Add 1 drop of very dilute iodine solution

(about 0.01 N). A blue coloration indicates starch. Certain papers not sized with starch will give a faint violet coloration, but this should be disregarded.

NOTE.—Applying iodine solution directly to the paper may give misleading results.

Quantitative Determination.—GLUE.—Weigh 3–5 grams of the paper, tear into small pieces, and place in a 500-cc. Kjeldahl digestion flask. Determine the nitrogen by the Gunning method as described on page 88. Calculate to glue by multiplying the nitrogen found by 5.6.

ROSIN.—Cut 5 grams of the paper into strips approximately $\frac{1}{2}$ inch wide and fold in numerous small crosswise folds. The folding is essential to secure complete and quick extraction. Do not tear the paper into small pieces, since it will then stick together and not be completely extracted. Place the folded strips in a Soxhlet extractor* and fill the latter with acidulated alcohol. This is made by adding to 100 cc. of 95% alcohol (specially denatured formula No. 30) 10 cc. of acidulated water, consisting of 5 cc. of glacial acetic acid to 100 cc. of water, and thoroughly mixing. Connect the extractor to an unweighed Soxhlet flask; add sufficiently more of the acidulated alcohol to insure having the flask about $\frac{1}{4}$ full. When the extractor is filled, start the extraction and siphon at least ten times.

Wash the alcoholic extract into a beaker and evaporate to 10 cc. or less on the steam bath. Cool, take up in about 25 cc. of ether and transfer to a 300-cc. separatory funnel containing about 150 cc. of water, to which has been added a little salt to prevent emulsion. Shake thoroughly and allow to separate. Draw off the water into a second separatory funnel and repeat the treatment with a fresh 25-cc. portion of ether. Combine the ether extracts which contain the rosin and wash twice with 100-cc. portions of water or until the ether layer is perfectly clear and the line between the ether and the water sharp and distinct.

If glue, which is extracted from the paper by the alcohol, should interfere by emulsifying with the ether, wash the combined ether extracts with a 10–15% NaCl solution (twice if nec-

* The Underwriters' Laboratory Rubber Extractor shown on page 752 may be used to advantage in place of a Soxhlet.

essary), and then wash with three 100-cc. portions of distilled water to remove the NaCl.

Finally transfer the ether extract to a weighed Soxhlet flask and evaporate off the ether. Dry at 100° C. in a water oven for exactly 1 hour. Cool in a desiccator and weigh.

STARCH.—Prepare from the paper a solution containing approximately 1% of reducing sugar (dextrose).* This solution must not contain *over* 1% and if, after the analysis is completed, it is found that this limit is exceeded, the analysis must be repeated, using a smaller amount of paper. The procedure is as follows:

Weigh carefully 3–5 grams of the paper, cut in very small pieces (about $\frac{1}{8}$ inch square), into a 250-cc. Erlenmeyer flask; add 150 cc. of water, and boil for about 5 minutes. Cool to about 50° C. and shake violently until the fibers are well separated. Then add 10 cc. of filtered saliva solution (see note 1 below). Place the flask in a water bath at 40–50° C. and stir frequently for 1 hour; then add 1 drop of 0.1 N iodine solution. If there is no indication of starch being present (blue color), filter on a Gooch crucible and wash with hot water. Transfer the filtrate, which should have a volume of about 200 cc., to a beaker; add 15 cc. of dil. HCl (5 : 4) and boil gently for 45 minutes, covering the beaker with a watch glass. Cool immediately. Nearly neutralize the acid with NaOH and complete the neutralization with Na_2CO_3 and litmus paper. Filter the neutral solution into a 250-cc. volumetric flask; make up to the mark, and determine the dextrose in 50 cc. according to the Allihn method on page 556.

The weight of dextrose multiplied by 0.9 gives the weight of starch. Multiply this weight by 5, divide by the weight of paper taken and multiply by 100 to obtain the percentage of starch in the paper. At least two 50-cc. portions of the neutral dextrose solution should be thus analyzed and the average result taken.

NOTES.—(1) The saliva is obtained by chewing paraffin wax and collecting the saliva in a beaker. Then add $\frac{1}{2}-\frac{2}{3}$ its volume of water and filter. The saliva should be tested with starch to be sure that it is active.

(2) This method depends upon the fact that the diastase in saliva will hydrolyze starch but will not hydrolyze the cellulose of paper. It some-

* Papers sized with starch in the beaters generally contain less than 2% of starch. Those tub-sized with starch may contain considerably more.

times happens, however, that saliva is not active towards starch and it should, therefore, always be tested by running a blank on a little starch and noting by means of the iodine test whether the starch is completely hydrolyzed.

Detection of Faulty Sizing.*—Draw a strip of the paper over the surface of an iron tannate ink (p. 471) and allow it to drain and dry naturally. Examine the inked surface under the microscope. A well-sized paper will show no indication of the fiber having absorbed ink, and the entire surface will be uniformly and lightly colored, as indicated in Fig. 28. In more poorly sized paper blotches of fibers absorb the ink, as shown in Fig. 29 and Fig. 30. Fig. 30*b* shows water-leaf filter paper, indicating by the darker colors that the fibers have absorbed the ink.

NOTES.—(1) All the papers shown in these plates (except Fig. 30*b*) are, according to the ordinary methods of testing, well-sized and practically identical.

(2) A paper well-sized throughout should also show a uniform coloring when the surface has been rubbed with an ink eraser, the loose particles brushed off, and the paper treated with ink as above.

TARNISHING TEST FOR PAPER

General.—A paper which is to be used for wrapping silverware should be essentially free from active sulfur compounds. If it is to be used for wrapping steel cutlery, the exclusion of active sulfur compounds need not be quite so rigid, but the paper must be free from acid and reasonably free from sulfur compounds. The determination of the total amount of sulfur in a paper is of little value in judging its suitability for anti-tarnish use, not only because the amount of sulfur is usually small, but there is no way of telling from the total sulfur determination what proportion is in an active form which would cause tarnishing.

Of the following methods, Method 1 was devised in this laboratory and Method 2 is essentially the method proposed by E. Sutermeister.† In testing papers by either method it is very essential to keep them away from all dust and laboratory fumes and in preparing the samples the fingers must be scrupulously clean and the papers not handled any more than absolutely necessary.

* *United States Dept. of Agr., Bur. Chem. Cir.* 107.

† *Pulp and Paper Mag.*, 1021 (1917).

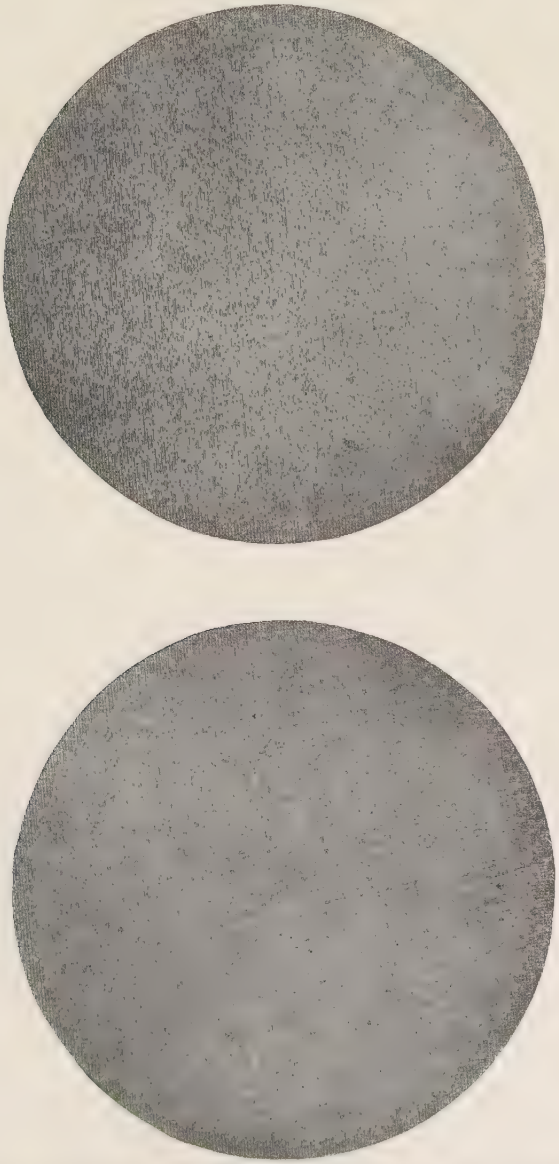


FIG. 28.—Appearance of Well-sized Paper after Test with Iron Tannate Ink.

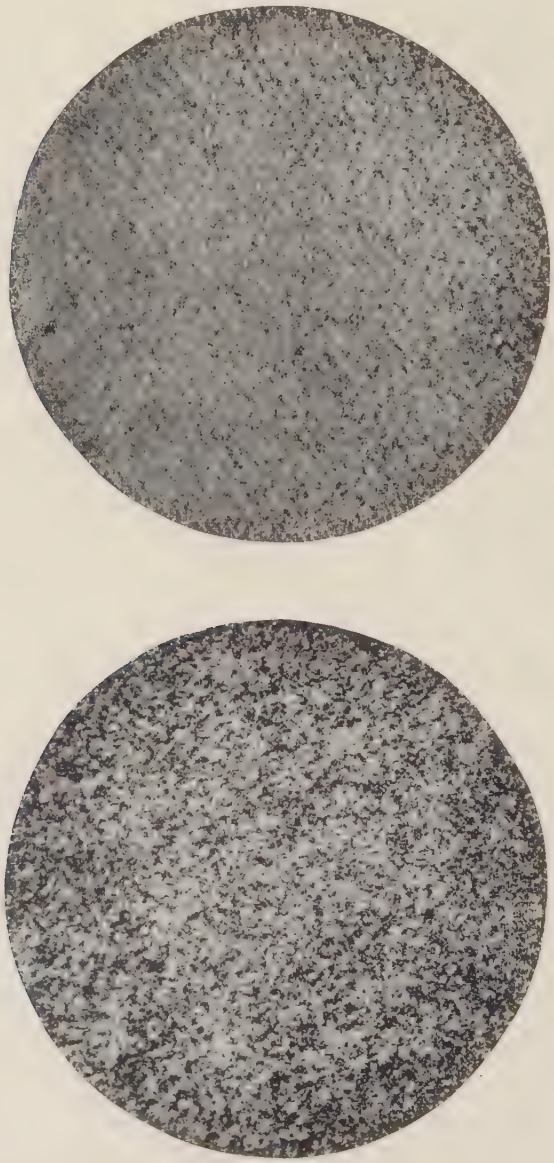


FIG. 29.—Appearance of Poorly-sized Papers in Which Blotches of Fibers Absorb the Ink.

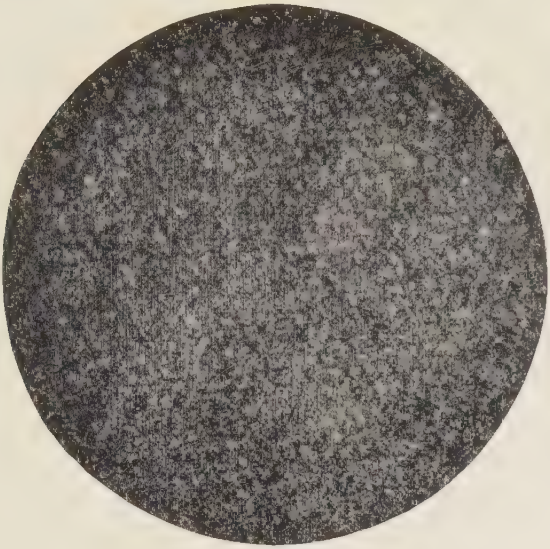


FIG. 30*a*.—Appearance of Paper with Inferior Sizing.

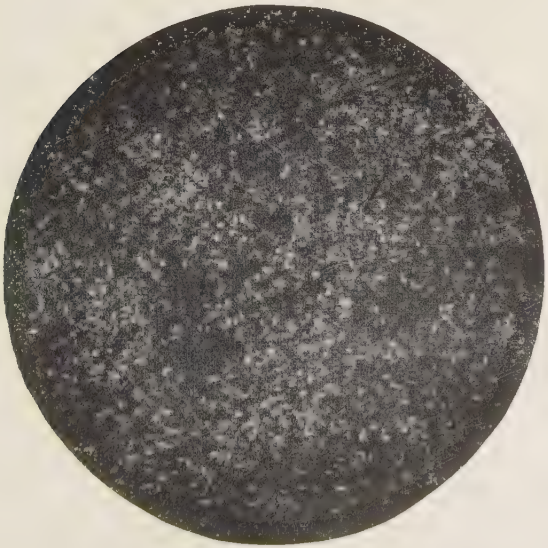


FIG. 30*b*.—Water-leaf Filter Paper, Showing Ink Absorbed.

Method 1

General.—The method consists of comparing the sample with special papers impregnated with 0.001% and 0.0001% Na_2S solutions, the sulfide test in each case being made under prescribed conditions by a hydrogen evolution method and lead acetate paper.

Preparation of Special Impregnated Papers.—Make the special papers from 9-cm. best white filter paper, each of which weighs approximately 0.6 gram. Prepare the following solutions:

(*a*) Dissolve 3 grams of *fresh* sodium sulfide crystals in 100 cc. of distilled water. (3 grams of $Na_2S{\cdot}9H_2O$ are equivalent to 1 gram of Na_2S.)

(*b*) Dilute 1 cc. of solution (*a*) to 1 liter to make a 0.001% Na_2S solution.

(*c*) Dilute 10 cc. of solution (*b*) to 100 cc. to make a 0.0001% Na_2S solution.

Saturate the filter paper in solutions (*b*) and (*c*) and dry in air. Considerable quantities of these papers may be made at one time and stored in separate, tightly stoppered bottles labeled:

"0.001% Na_2S Paper for Tarnishing Test."

"0.0001% Na_2S Paper for Tarnishing Test."

The papers may also be torn into 4 equal segments, each segment (0.15 gram) being sufficient for one test.

Materials Required.—(1) Four 500-cc., flat-bottomed flasks, approximately 7 inches high; (2) Granulated zinc (arsenic free); (3) 15% HCl solution; (4) Lead acetate test paper, moistened; (5) Absorbent cotton.

Procedure.—Into each flask put 2 grams of granulated zinc and 0.15 gram of paper torn into small pieces. The 4 flasks are for the following papers: (1) Sample; (2) Pure filter paper (for a blank); (3) 0.001% Na_2S paper; and (4) 0.0001% Na_2S paper.

Add to each flask 25 cc. of 15% HCl (free from As). Into the neck of the flask insert a loose plug of cotton to a depth of about $1\frac{1}{2}$ inches. Above the cotton place a piece of moistened lead acetate test-paper about 1 inch square, and cover this loosely with a final plug of cotton. Set the 4 flasks in a pan or tub containing water at room temperature to a depth of $\frac{1}{4}$–$\frac{1}{2}$ inch, in order to prevent any considerable rise in the temperature

of the contents of the flasks. The liberated hydrogen will carry any H_2S evolved up to the lead acetate paper, which will darken. Examine the 4 lead acetate papers at the end of 30, 60 and 90 minutes and record their comparative appearances.

Interpretation of Results.—It has been found that the 0.001% Na_2S paper causes some tarnishing when held in contact with a polished 10-cent piece for 5 weeks. Commercial papers known to have caused tarnishing of polished metal goods have been found to be more reactive under this test than the 0.001% Na_2S paper. Therefore, a paper to be acceptable should show up as well as the 0.0001% Na_2S paper (which should show slight discoloration in about 60 minutes). A paper between 0.0001% and 0.001% Na_2S papers is dangerous; while those that are inferior to 0.001% Na_2S paper should be unquestionably rejected.

In reporting, a paper superior to 0.0001% Na_2S paper should be classed as "safe"; those between 0.0001% and 0.001% Na_2S as "questionable"; and those inferior to 0.001% Na_2S as "unsafe."

NOTE.—In judging papers which are to be used solely for wrapping steel cutlery, a paper which is free from acid and shows less sulfur than the 0.001% Na_2S standard may be classed as safe.

METHOD 2

Apparatus.—The apparatus consists of a 500-cc., round-bottomed flask with a neck about 2 inches long and 1 inch in diameter. The mouth of this neck is ground to a flat surface and on this is placed a glass tube about 4 inches long and 1 inch in diameter, the lower end of which is also ground flat to fit tightly upon the upper surface of the neck of the flask. The whole is so arranged that after placing a piece of filter paper between the two ground surfaces the tube and flask may be securely clamped together so that all gas generated in the flask must pass through the filter paper and then up through the superimposed glass tube.

Procedure.—In the case of tissue papers take a sample of 25 square inches and determine its weight; in the case of heavy papers weigh out 0.25 gram. (The paper should be handled as little as possible with the fingers, particularly if they are moist.) Shake up in a wide-mouthed, glass-stoppered bottle with 10 cc. of distilled water. When partial disintegration has taken place

add another 10 cc. of water and continue shaking until the paper has been completely reduced to pulp. Transfer the larger part of the pulped mass to the flask and rinse the residue which is left in the bottle into the flask with a mixture of 10 cc. of sulfur-free H_3PO_4 and 20 cc. of water.

Prepare turnings from the highest grade, pure stick Zn, which must be free from S and As. Treat 1 gram of these turnings with 10 cc. of a dilute solution of $CuSO_4 \cdot 5H_2O$ (0.1 gram dissolved in 100 cc. of water is a suitable strength). After a few minutes all the Cu will have deposited. Finally wash the turnings thoroughly to remove every trace of $ZnSO_4$, add the turnings to the flask and insert a wad of cotton in the neck. Then clamp between the 2 ground glass surfaces a piece of filter paper about 2 inches square which has been perforated with small pin holes about $\frac{1}{8}$ inch apart and which just before use is moistened with several drops of lead acetate solution. Finally place a loose wad of cotton in the tube above the paper.

Place the flask on the steam bath and let stand with occasional shaking for 1 hour. Then remove the filter paper from the neck of the flask and dry it in air. Compare it with standard test pieces by placing them side by side on a piece of white paper and covering them with a thin piece of clear white glass.

Standard Test Pieces.—Prepare the standard test pieces as follows: Place 0.25-cc. portions of S-free cotton in flasks in place of the paper pulp and add to each measured amounts of a very weak solution of sodium thiosulfate the strength of which is accurately known.

Sulfur-free cotton is prepared by boiling absorbent cotton in 1% NaOH solution and washing thoroughly with distilled water.

Thiosulfate solution is prepared as follows:

(*A*) Dissolve 3.88 grams of $Na_2S_2O_3 \cdot 5H_2O$ in water and dilute to 1 liter. 1 cc. of this solution is equivalent to 0.001 gram of S.

(*B*) Add 10 cc. of Solution *A* to about 500 cc. of water contained in a liter volumetric flask. Dilute to the mark and mix thoroughly. 1 cc. of this solution is equivalent to 0.00001 gram of S.

(*C*) Dilute 10 cc. of Solution *B* in the same manner to 1 liter in a volumetric flask. 1 cc. of this solution is equivalent to 0.0000001 gram of S.

Solution *C* is to be used for preparing the standard papers. Convenient quantities to be added to the flask are 10, 20, and 50 cc., respectively, equivalent to 0.000001, 0.000002, and 0.000005 gram of sulfur. The standard test-papers prepared from known amounts of sulfur must be freshly made each time the tests are carried out. A blank should also be run to make sure that the H_3PO_3 and Zn give no test for sulfur.

Interpretation of Results.—If has been found that 0.000001 gram of S in the flask will give a distinct color on the lead acetate paper. A paper which does not contain more than 0.000002 gram of active S in 0.25 gram of paper may be considered safe for wrapping silverware. A paper containing more than this amount, but not more than 0.000005 gram, should be considered questionable for silverware but if it is not acid should be suitable for steel cutlery.

FILTER PAPER

General.—The essential qualities of a good filter paper are: (1), retention of precipitates; (2) speed of filtration (penetrability); (3), low ash content (in quantitative paper); (4), good folding properties and strength; (5) good formation, *i.e.*, freedom from "wildness" and excessive knots or clumps of fiber; (6), freedom from dirt specks and pin holes.

Ash.—Weigh 2 separate portions of 10 circles each and calculate the average weight per circle. Then tear the 2 samples into small pieces, place in 2 large, weighed, porcelain crucibles and smoke off the paper without letting it actually take fire, keeping the crucible loosely covered. Finally ignite the ash as nearly white as possible over a Meker burner or in a muffle at bright red heat, cool in a desiccator and weigh. Calculate the ash both in percentage and in decimal of a gram per 11-cm. circle. The average ash of 2 duplicate determinations which agree reasonably well should not be over 0.00015 gram per 11-cm. circle on high-grade quantitative paper.

Retention of Barium Sulfate.—Place 20 cc. of approximately normal H_2SO_4 in a 50-cc. beaker and heat until ebullition just commences. Then add from a burette 20 cc. of approximately normal $BaCl_2$ solution, with the flame still under the beaker, at the rate of 1 cc. per second. At the end of 20 seconds, remove

the beaker and pour the contents upon the filter paper folded and fitted in a funnel. From the clarity or cloudiness of the filtrate the paper is judged as to its retention of $BaSO_4$.

Solutions.—Normal H_2SO_4.—Weigh out 52.1 grams of conc. H_2SO_4 (94%), transfer to a liter flask about $\frac{1}{2}$ full of distilled water, dilute to the mark and mix thoroughly.

Normal $BaCl_2$ Solution.—Weigh out 122 grams of $BaCl_2 \cdot 2H_2O$, dissolve in distilled water and dilute to 1 liter.

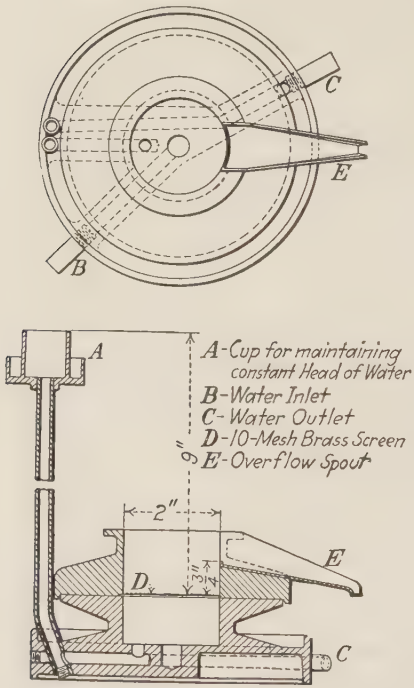


Fig. 31.—Penetrability Tester for Filter Paper.

Penetrability.—The penetrability is measured by the number of seconds required for 100 cc. of distilled water at approximately 20° C. to pass through the paper under a definite head. Any form of apparatus which will insure a constant head of water may be used for comparison purposes. We have found the penetrability tester shown in Fig. 31 (devised in this laboratory) works very satisfactorily. The shaded portions may be cast from lead. The constant head is maintained by opening the stop-cock from the reservoir just wide enough to keep the water level with the top of the vertical pipe. When this condition is obtained, place a 100-cc. graduate under the spout and measure the time in seconds required for the graduate to fill to the 100-cc. mark. Run at least 5 tests, each on a different portion of the paper or on a different circle, and report the average result.

Thickness.—Determine the thickness with a standard thickness tester at 5 different points on the paper.

Note.—The thickness tests on filter paper are of questionable value, as most papers have a finish similar to embossing which makes it doubtful if the reading of the gage gives the true thickness of the paper sheet.

Bursting Strength.—Determine the bursting strength with the small Mullen tester. Run at least 5 tests and report the average.

WHITE WATER

General.—Broadly speaking, there are 2 classes of waste water in paper mills which are generally termed White Water: (1) the returned water from pulp thickeners, which is used to supply grinders, sliver screens or in such other ways as may save its fiber content; (2) the water extracted from the paper stock on the machine by the wire, suction boxes and presses and returned to the system in order to save the filler, coloring matter, alum, size or fibers contained in it. This is more properly known as Back Water.

The name White Water is derived from the color, due to the finely divided material in suspension. In some mills the white water is used repeatedly, while in others merely the fibers are recovered in "save-alls" and the rest run to the sewer.

Usually the only determinations required on white water samples are the amounts of fiber and filler. Results should be expressed in pounds per 100,000 gallons.

Fiber.—Shake the sample thoroughly and pour off quickly 1 liter, or an aliquot of a liter, depending upon the consistency of the sample. Filter on a quantitative filter paper which has been dried at 105° C. and weighed in a weighing bottle. (The filter paper should be dried to constant weight but should not be heated unnecessarily long on account of danger of rendering it brittle.) Wash all the fibers and suspended matter upon the filter with distilled water and then wash once or twice on the filter. Dry the filter and contents to constant weight in the weighing bottle at 105° C. Multiply the weight in grams per liter by 834. This gives the total suspended matter in pounds per 100,000 gallons. Subtract from this the amount of filler as later determined and report the difference as Fiber.

Filler.—Transfer the filter paper and contents to a weighed platinum crucible, ignite to a white ash, cool in a desiccator and weigh. Report the weight, expressed in pounds per 100,000 gallons, as Filler—calculated from ash.

NOTE.—In some laboratories it is customary to evaporate a known amount of the sample directly to dryness and weigh the residue and then ash

it. As most white waters contain alum and size, this procedure does not give correct results. The alum if ignited strongly is converted to Al_2O_3 and the organic matter of the size is burned off and included in the fiber. An analysis made in this way gives higher results for filler and also for fiber. The natural dissolved solids of the water are also thus included as filler.

COTTON CELLULOSE (COTTON LINTERS) FOR NITRATION

General.—U. S. Navy Specification 65C5, July 10, 1913, requires that cotton for nitrating for smokeless powder shall contain not over 7% of water, not over 0.4% of ether extract, not over 0.8% of ash and only traces of lime salts; and that it shall be free from hypochlorites, dirt, and foreign matter. This is essentially the same as the Joint Powder Specifications which require the use of a bleached cellulose containing not more than 0.4% of extractive matter, not more than 0.8% of ash, and state that it should not contain more than "traces" of lime, chlorides, and sulfates.

For some commercial grades of nitrocellulose unbleached cotton is used, but the methods of analysis are the same as for bleached cotton.

The routine analysis of cotton includes the determinations of moisture, ether extract, ash, solubility in 95% H_2SO_4 and solubility in 10% KOH solution. The furfural value is also frequently determined, and on crude fiber the amount of "dust" is determined by a sieving test. It is also sometimes desirable to determine the copper number and the amount of starch.

Sampling.—In sampling fiber in bales, take a section extending from one side to approximately the center from each bale sampled, and take samples from not less than 10% of the bales in the lot. In sampling crude fiber, make special note of, and take samples from, any bales showing large proportions of moldy fiber or of very oily fiber, as indicated by a strong yellow color.

Blend the samples for moisture quickly and thoroughly by hand and place a sample of about 20 grams in a previously weighed glass or tin vessel with a tightly fitting cover. Open up the remainder of the sample by hand, or in a mill or picker if available, and after being thoroughly blended, reduce to proper size by quartering, and dry at 105° C.

Make all determinations, except moisture and dust, on the dry sample.

Moisture.—Take about 20 grams of the sample prepared for moisture determination and weigh under conditions to avoid changes in moisture content. Dry at 105° C. for 3 hours, or if the moisture is high, as may happen with samples taken from bales that have been exposed to rain, until constant weight is reached. Calculate the loss in weight to percentage of the sample as received.

NOTE.—Instead of determining the moisture on a large scale and using portions of this dried material for subsequent tests, it is permissible to run the tests on the sample as received and calculate results to the dry basis, provided, however, that the moisture is not excessive (5–10%) and that the sample is kept where it does not lose or gain moisture.

Ash.—Place at least 5 grams of the dry material, prepared as above, in a platinum or fused silica dish of 80–100-cc. capacity and ignite in a muffle or over a burner to complete incineration at a low red heat, taking care to avoid loss of ash by air currents during handling. Finally cool the dish and contents in a desiccator and weigh. Calculate the result to percentage of the dry weight of the cotton.

NOTE.—The Powder Specifications call for the digestion of a 1.5-gram sample with a little pure HNO_3 and incineration at a red heat. The use of the smaller sample of cotton and a higher temperature of incineration, however, is likely to give lower results.

Ether Extract.—Extract thoroughly about 5 grams of the dry material with pure ethyl ether in a suitable extraction apparatus (preferably Knorr's; see Eimer & Amend *Catalog*, No. 3185) for about 8 hours or until further extraction removes no additional substances soluble in ether. Weigh the extractive matter after drying at 100° C. to constant weight, and calculate the result (after deducting the weight of any residue in the ether) to percentage of the dry weight of the material. Take care to have the extractive matter free from fine particles of fiber which may be carried through mechanically. After extraction with ether, the sample may be dried and used for the determination of non-cellulose, as below.

Non-cellulose.—The H_2SO_4 used must be within 0.5% of 95% strength. Make the determination by treating 5 grams of the dry sample at about 20° C. with 50 cc. of the acid at the same

temperature. In the case of crude fibers, it is important to remove the oils by extraction with ether before making this determination. Stir the fiber vigorously in the acid for 5 minutes, then slowly pour into 1 liter of cold distilled water. Heat the aqueous solution on a hot plate for at least 4 hours, with frequent stirring. It is important to keep the temperature at 99–100° C. and to maintain the level of the liquid constant. Then filter out the insoluble matter on a weighed Gooch crucible with a carefully prepared asbestos mat. Thoroughly wash the contents of the Gooch crucible with boiling distilled water to remove the last traces of H_2SO_4 and then dry for 3 hours at 102–105° C. Cool and weigh the non-cellulose and calculate the result to percentage on the dry weight taken. It is important to have the fiber well opened up and free from lumps, as, if lumps are present, a higher result may be expected.

Approximate Cellulose.—Calculate the "approximate cellulose" in the fiber by adding together the percentages of ash, ether extract, and non-cellulose and subtracting from 100%.

Solubility in Caustic.—Cellulose is insoluble in alkalies, so that in a crude fiber the solubility in KOH or NaOH is a measure of the non-cellulose present. In a purified fiber it is a measure of the severity of bleaching, and indicates the amount of hydrocellulose and oxycellulose present.

Prepare a solution of pure KOH within 0.1% of 10% concentration by dissolving the proper weight of the purest obtainable KOH in distilled water.* Carefully check the strength of the solution by titration with standard acid and phenolphthalein. It must be carefully protected from CO_2, as carbonates do not act.

Dry approximately 2 grams of the sample in a wide-mouthed weighing bottle to constant weight at 102–105° C., transfer the contents of the bottle to a 250-cc. Pyrex glass or porcelain beaker, add 100 cc. of the solution, cover with a watch glass and heat at 100° C. for 3 hours. Heating on a steam bath is not satisfactory for this purpose, as it does not give a sufficiently high temperature. Care must be taken to avoid concentration of the solution or undue oxidation of the fiber due to exposure of the alkali-soaked fiber to the air. It is important that the temperature be kept

* A solution of pure NaOH within 0.1% of 7.14% may be used instead of a 10% KOH solution.

within 99–101° C., since variations in temperature affect the result materially.

After the heating is completed, pour the contents of the beaker into a 2-liter beaker containing 1 liter of distilled water and wash any residue in the small beaker into the larger. Then neutralize the alkali with a decided excess of acetic acid, the excess of acid being necessary in order to break up the combination of alkali and cellulose. Filter the undissolved cotton into a weighed Gooch crucible having an asbestos mat and thoroughly wash successively with hot water, alcohol and ether. Then dry rapidly to constant weight at 102–105° C. Calculate the loss of weight to percentage of the dry material.

NOTE.—In making this determination on crude fiber, the amount soluble in hot water alone is deducted from the total and expressed separately, and a further correction must be made for the percentage of oils extracted by ether and the percentage of ash which goes into solution in the acetic acid, though these corrections are not necessary on bleached fibers. In order to determine the amount of ash which goes into solution, an ash determination must be made on the fiber after treatment.

Furfural Value (Pentosans).—*Preparation of Reagents.*—Test the purity of the phloroglucinol by dissolving a small quantity in a few drops of acetic anhydride, then heat almost to boiling and add a few drops of conc. H_2SO_4. A violet color indicates the presence of diresorcin. If the phloroglucinol gives more than a faint coloration, it should be purified by the following method:

Heat in a beaker about 300 cc. of 12% HCl and 11 grams of the commercial phloroglucinol. Add the latter in small quantities at a time, stirring constantly until it has almost entirely dissolved (some impurities may resist solution). Pour the hot solution into a sufficient quantity of the same HCl (cold) to make the volume 1500 cc. Let stand at least overnight, preferably several days, to allow the diresorcin to crystallize out, and filter immediately before using. The solution may turn yellow, but this does not interfere with its usefulness. In using, add the volume containing the required amount to the distillate as obtained below.

The 12% HCl is prepared by adding 1 volume of conc. HCl to 2 volumes of water. Determine the strength by titration with standard alkali and adjust to 12% by adding more water or acid if necessary.

Determination.—Place a weighed quantity of the material, chosen so that the weight of furfural phloroglucid obtained shall not exceed 0.300 gram, in a 300-cc. distillation flask together with 100 cc. of 12% HCl and several pieces of recently ignited pumice stone. Place the flask on a wire gauze, connect with a condenser, heat rather gently at first, and so regulate as to distill over 30 cc. in about 10 minutes, the distillate passing through a small filter paper. Replace the 30 cc. distilled by a like quantity of the 12% HCl, added by means of a separatory funnel in such a manner as to wash down the particles adhering to the sides of the flask, and continue the process until the distillate amounts to 360 cc. To the total distillate gradually add a quantity of phloroglucinol (purified if necessary) dissolved in 12% HCl and thoroughly stir the resulting mixture. The amount of phloroglucinol used should be about double that of the furfural expected.

The solution first turns yellow, then green, and very soon an amorphous greenish precipitate appears, which grows rapidly darker, till it finally becomes almost black. Make the solution up to 400 cc. with 12% HCl and let stand overnight.

Filter the amorphous black precipitate through an asbestos felt in a Gooch crucible which has been previously dried and weighed in a weighing bottle. Wash carefully with 150 cc. of water in such a way that the water is not entirely removed from the crucible until the very last, then dry for 4 hours at the temperature of boiling water, cool and weigh in the weighing bottle as furfural phloroglucid. Calculate to furfural or pentosans, as required, using the following formulæ given by Kröber:

(*a*) For a weight of phloroglucid, w, less than 0.030 gram: Furfural $= (w+0.0052)\times 0.5170$. Pentosans $= (w+0.0052)\times 0.8949$.

(*b*) For a weight of phloroglucid, w, more than 0.300 gram: Furfural $= (w+0.0052)\times 0.5180$. Pentosans $= (w+0.0052)\times 0.8824$.

(*c*) For a weight of phloroglucid, w, between 0.030–0.300 gram: Furfural $= (w+0.0052)\times 0.5185$. Pentosans $= (w+0.0052)\times 0.8866$.

Copper Value.—Cut 3 grams of the sample into small pieces and mix with 150 cc. of boiling water. Heat to boiling 50 cc. of

Fehling's copper solution and 50 cc. of Fehling's alkaline tartrate solution* and add to the sample. Then boil the whole with continuous stirring for 15 minutes, filter and wash with hot water. Warm the residue with dil. HNO_3, to dissolve out the absorbed Cu, and filter. Determine the Cu electrolytically on a rotating cathode. Calculate the Copper Value or Copper Number, which is the weight in grams of metallic Cu thus obtained per 100 grams of dry material.

NOTES.—(1) When this determination is used as a basis of acceptance or rejection, 6 samples shall be selected from various parts of the bale. The copper value of each of these samples shall be determined as above and the highest copper value of each of the 6 shall be considered the copper value of the lot.

(2) Most specifications require that the copper value shall not exceed 2.

(3) The copper value is a measure of the oxy-cellulose and indicates whether the material has been overbleached. Mitchell and Prideaux ("Fibers in the Textile Industry," p. 93) give representative copper numbers as follows:

Surgical cotton wool	1.6
Parchment paper	4.2
Bleached sulfite pulp	3.9
Overbleached sulfite pulp	19.3

Starch.—Boil 5 grams of the sample (well teased, if it is cotton; cut up into small pieces, if it is waste) in 300 cc. of water for 6 hours, changing the water every hour, and concentrate the combined washings so that they may be made up to either 250 or 500 cc. Place 50 cc. of this solution in a Nessler tube and add 0.001 N iodine solution drop by drop to produce the maximum blue tint. Compare the color with colorimetric standards prepared from a standard starch solution. If the color produced by the 50 cc. of the cotton extract is too dark, a lesser quantity should be taken.

Standard Starch Solution.—Grind 0.1 gram of dry corn starch with water in a porcelain mortar and wash into 300 cc. of boiling water. Boil for 15 minutes, cool, and make up in a volumetric flask to 500 cc.

NOTES.—(1) The blue color from extracted cotton changes to violet on standing, and the comparison therefore should be made quickly.

(2) The method is applicable to concentrations ranging from 0.02 to 0.008% of starch.

* Use the Soxhlet modifications (see p. 3).

REFERENCES.—Part of the above method was originally furnished us by W. F. Allen of the Meridian Cellulose Co., and is the method used by E. I. Du Pont de Nemours & Company. The procedure for Furfural Value is the official method of the Association of Official Agricultural Chemists, published in its "Methods of Analysis," 120 (1925).

WOOD DISTILLATE PRODUCTS

General.—The chief hard woods used in this country for distillation are beech, birch, and maple. The products of distillation are gas, crude pyroligneous liquor, and charcoal. This method is concerned only with the analysis of the crude liquor, which consists essentially of acetic acid, crude wood alcohol, tar, and water.

ANALYSIS OF CRUDE LIQUOR

Tar.—In commercial practice the bulk of the tar is mechanically separated, but the liquor always contains more or less dissolved or suspended tar.

Weigh the whole sample and determine its volume. Separate mechanically as much of the tar as possible, weighing the amount thus separated. If desired, its sp. gr. may be determined by the Westphal balance or a pycnometer.

Determine the dissolved tar as later described and add the amount to the amount obtained by mechanical separation.

Acetic Acid.—Place 100 cc. of the liquor in a weighed retort or distilling flask, set up in an oil bath and connect with a Liebig condenser. Place a thermometer in the oil and gradually heat the oil bath to 140° C., collecting the distillate in a 250-cc. volumetric flask. Keep the temperature of the bath at 140° C. until nothing more comes over. In the flask there will remain about 10 cc. of tar which still contains some acetic acid. The last traces of acid must be blown over by a current of steam, keeping the oil bath at 150° C. and collecting the distillate in the flask with the main distillate. Make up the distillate to the mark at 15.5° C. Pipette out 50 cc. at the same temperature and titrate with N NaOH and phenolphthalein. Calculate to acetic acid and to calcium acetate.

CALCULATIONS.—1 cc. N NaOH = 0.06003 gram $HC_2H_3O_2$.
= 0.07906 gram $Ca(C_2H_3O_2)_2$.

NOTE.—For ordinary purposes, instead of blowing over the last traces of acid with steam, satisfactory results can be obtained by cooling down the flask, adding 50 cc. of water, and again distilling until nothing more comes over at 140° C. (See *U. S. Dept. Agr., Forest Service, Bull.* 129, 6.)

Dissolved Tar.—The residue in the flask from the distillation of the acetic acid represents the dissolved tar. Cool and weigh, and add the amount to the tar mechanically separated above.

Crude Wood Alcohol.—Place 1 liter of the crude liquor in a round-bottomed, 1500-cc. flask. Set the flask in an oil bath and connect to a vertical condenser. Distill until 500 cc. of distillate have been collected. Neutralize the distillate with NaOH and distill again from a smaller flask until 50% has distilled off (250 cc.). This distillate is still too dilute to estimate the alcohol accurately, especially as it still contains methyl acetate which, owing to its high sp. gr., would make the results come low. Hence, the distillate should again be neutralized with NaOH and redistilled, collecting in a 100-cc. volumetric flask. Stop the distillation just before 100 cc. have come over, cool to 15.5° C. and make up to volume accurately with distilled water. Determine the sp. gr. of the distillate at 15.5° C. with a Westphal balance, or preferably with a pycnometer. From the sp. gr. calculate the percentage of methyl alcohol in this distillate, both by weight and by volume, and figure back to the original sample (see p. 653).

NOTES.—(1) Great care must be exercised in making the distillation not to lose alcohol. A vertical condenser is preferable to a horizontal one and the end of the condenser should run well down into the neck of the flask.

(2) By this method all the substances which accompany methyl alcohol, such as acetone, acetaldehyde, allylalcohol, etc., are calculated as methyl alcohol. The results, therefore, should be reported as Crude Wood Alcohol and, if the determination of the true methyl alcohol content is desired, use the method of Zeisal and Stritar. (*Zeit. anal. Chem.*, **29,** 359; **42,** 579; **43,** 387.)

ANALYSIS OF PRODUCTS OF CRUDE LIQUOR

Acetic Acid.—Two kinds of acetic acid from wood are recognized:

(1) Crude wood acid, containing about 6% of acetic acid.

(2) Rectified wood acid, so-called "light vinegar," which has a similar strength.

The first product is obtained from the crude wood liquor by distilling off the alcohol and diluting the residue in the still with

water until it has an acid content of 6%. The second product is made from a single distillation of the crude wood acid, which yields a pale yellow liquid still containing about 6% of acid.

The determination of the strength of the acetic acid can be made in the case of tar-free wood acid (product 2) by titrating with N NaOH and phenolphthalein. In the case of the raw acid, however, the end-point is often difficult to obtain with certainty and it is best to dilute it 1:10 before attempting titration.

The tar contained in crude liquor gives a strong coloration with NaOH and it is often impossible to get an accurate titration. This may be overcome by using litmus or phenolphthalein as an outside indicator on a white porcelain tile. For accurate results, however, it is preferable to make a distillation and titrate the distillate as described in the first part of the method.

Acetone.—The acetone content of crude wood alcohol is determined by the well-known Messinger method, which is described on page 95.

Total Ketones.—For general purposes a determination of the acetone content, as obtained by the Messinger method, gives sufficient information. In case the total ketone content is desired, the method of Denigès (*Comp. rend.* **127,** 963) may be employed.

CHAPTER IX

ANALYSIS OF TEXTILES AND TEXTILE FIBERS

STRUCTURAL ANALYSIS OF TEXTILE FABRICS

General.—The following is a brief outline of the determinations usually desired in making structural analyses and physical tests of textile fabrics and a description of the procedures employed.

Fiber Composition.—See page 504.

Ash (Mineral Weighting).—Determine the ash on 2–5 grams of the sample in a porcelain crucible and report the percentage as Mineral Weighting. The weighting usually consists principally of tin salts, Fe_2O_3, Prussian blue, SiO_2, and P_2O_5. Tin phosphate is not uncommon. The estimation of the mineral matter is of special importance in the examination of such fabrics as waterproof rain-coats, window shades, bookbinders' cloth, fireproof cloth, heavily weighed silks, etc. Black silks sometimes contain 250% of weighting, based on the weight of the silk.

NOTE.—In waterproof goods ammonium salts often occur and these, of course, would be volatilized in ashing and must be tested for on a separate portion.

Sizing Materials.—The sizing usually consists of starch, gums, glue, oil, fat or wax. Nearly all textiles will show the presence of small amounts of various sizing materials which it is necessary to use in dyeing and finishing in order to produce the desired feel and finish. It is seldom necessary to determine these quantitatively. Boiling hot water or a solution of "diastafor" will remove starch. Gums are also as a general rule soluble in water and so is glue. Oils and fats can be removed by ether extraction and waxes by alcohol extraction.

When the sizing consists of starch and British gum (dextrin), the amount may be determined as follows: Dry approximately 5 grams to constant weight at 100° C. Determine the loss. Boil the dried sample in water for 10 minutes. Rinse well and

digest for 2 hours at 60° C. in a solution of 15 cc. of commercial "diastafor" in 500 cc. of water. Wash well in hot water, boil for 1 hour in 500 cc. of water, wash again, dry at 100° C. and weigh.

$$\text{Calculation.—\% sizing} = \frac{\text{total loss} - \text{moisture loss}}{\text{weight of original sample}} \times 100.$$

Bursting Strength.—Determine the bursting strength on the Perkins Mullen tester (Fig. 25, p. 466). Take the average of at least 5 tests, and preferably 10.

Tensile Strength and Stretch.—There are 2 methods of determining tensile strength as follows:

Strip Method.—Cut pieces of the fabric, both in the warp and in the filling direction, each piece 8 inches long and $1\frac{1}{2}$ inches wide. Ravel down to the desired width, or the specified number of threads per inch, by removing approximately an equal number of threads from each side. Insert these strips in the test machine. (In case stretch is to be determined, 2 parallel marks should be made on the specimen 3 inches apart, and the lower edge of the jaws should be clamped even with these marks.) After clamping the jaws, apply power to the machine to make the separation of the jaws proceed at a uniform rate of 20 inches per minute.

From the breaking strength of the strip and its width calculate the tensile strength of the fabric in each direction in pounds per inch. Also measure the elongation or stretch at time of breaking between the lines drawn 3 inches apart. Express the stretch results in percentage on 3 inches.

Grab Method.—It is necessary to use this method in case of hosiery and knitted goods which cannot be raveled down. Tests should be made on the Scott tester. Test specimens should be 5 inches long by 2 inches wide and cut in each direction of the goods. On each piece as it lies flat, without tension on a smooth surface, draw pencil lines along the thread vertically and $\frac{1}{2}$ inch from each edge so that 1 inch of fabric will be between them. Then draw pencil lines along the thread horizontally and 1 inch apart in the center of the specimen. The clamps of the machine consist of 2 jaws, one at least 2 inches wide and the other 1 inch wide. Clamp the specimen in the 2 jaws of the machine securely, taking care that the threads being tested are parallel to the direc-

tion of pull, and the cross threads are at right angles to it. Have the length of the test specimen between the jaws exactly 1 inch. Report the tensile strength in pounds per inch and the increase in length of the 1-inch portion as the elongation, either in units of length or as a percentage of 1 inch.

NOTE.—On tensile and elongation tests make at least 5 and preferably 10 tests in each direction and report the averages.

Folding Endurance.—Materials such as silk, book-cloth, window shades, etc., are subject to folding to a considerable extent in actual use. In such cases a folding endurance test will show to what extent they may be expected to resist deterioration from this cause. Make the test on the Schopper folding machine (Fig. 17, p. 312). Cut strips from each direction about 30 mm. wide and ravel down until they are exactly 15 mm. wide. Insert in the machine and determine the number of double folds they will stand, under a tension of 1 kilo, before breaking. At least 5 tests, and preferably 10, should be made in each direction and the average figures reported.

Thread Count.—This term is used in reporting the number of threads per inch in the fabric in each direction. The greater the number of threads per inch, the finer or closer is the texture of the fabric. Count the threads in each direction with a special counting glass and report the number of threads in the filling as "picks per inch" and in the warp as "threads per inch." Make sure the fabric is flat and not under tension while counting.

Twist.—This term is used in determining the number of twists per inch in a thread. It is also customary to designate them as right or left twists. A yarn or thread is considered to have a right-hand or regular twist if, when it is held vertical, the spirals or twists are seen to incline upwards in a right-hand direction, and a left-hand or reverse twist when the spirals are seen to incline upwards in a left-hand direction.

Size of Yarn.—The terms "yarn number" and "size" are commonly used to indicate the length of yarn per unit of weight. There are many systems of numbering in use which are for the most part based on arbitrary quantities, differing according to the kind of material or the locality, or even the preference of the individual. For use in this laboratory, we have adopted the Fixed Weight System in which the count represents the length

(hanks or yards) of a fixed weight. In this system the count number is inversely proportional to the size of the yarn. The basis of a No. 1 yarn on the Fixed Weight System is shown in Table XXIII.

Table XXIII—Fixed Weight System of Yarn Numbers

Material	Unit	Usage
Woolen	1600-yard lengths per pound	Anglo-American
Cotton	840-yard lengths per pound	World
Worsted	560-yard lengths per pound	Anglo-American
Linen	300-yard lengths per pound	World

A No. 2 cotton would contain 2×840 yards per pound and a No. 3 cotton, 3×840.

Ply yarn is numbered to indicate the number of strands and the size of a single yarn, thus: 2–40 means that 2 strands of size 40 are placed together to form a 2-ply yarn. Spun silk is an exception to this rule, the first number indicating the count or size of the ply yarn and the second the number of strands, thus: 20–2 spun silk indicates that 2 strands of 40 size have been doubled or twisted, making a 2-ply yarn equal to a single 20.

Silk is usually numbered either by the dram or the denier system. The dram system represents the number of drams per 1000 yards; the denier system represents the number of grams per 10,000 meters. In the United States the denier system is used for raw silk and the dram system for thrown silk. To convert one into the other use the formula: Dram size×33.36 = denier size.

By weighing a given length of yarn it is possible to calculate the number of unit lengths per unit weight, and the size of the yarn. Conversely, the number of yards per pound may be calculated by dividing 4,465,000 yards by the denier size; *e.g.*, a 100-denier silk will run 44,650 yards to the pound.

Weight.—The weight of fabrics is reported as ounces per square yard. In case of hosiery it is reported as weight per dozen pairs of hose.

Weigh a piece of definite size and calculate the weight per square yard

CALCULATION.—Grams per square inch $\times 45.71 =$ ounces per square yard.

Special Tests.—(1) FASTNESS TO LIGHT.—The rational test for determining fastness to light of dyed goods is exposure to bright sunlight. This is not practical, however, as it requires too much time. A fairly satisfactory indication of the relative fastness to light can be obtained by exposing a small piece of the goods for 7 hours to ultra-violet light* and comparing with a piece of the original goods. In the case of very fast colors it is sometimes desirable to make a much longer exposure.

(2) FASTNESS TO WASHING.—(*a*) *Cotton.*—Dissolve 2 grams of Ivory soap in 1000 cc. of water and immerse a piece of the sample in a portion of this solution for $\frac{1}{2}$ hour at 60° C., together with a piece of white cotton and a piece of white woolen goods. If the color strips off the sample and stains the white material, it is not fast to washing.

(*b*) *Wool.*—Dissolve 2 grams of Ivory soap and 0.5 gram of $NaCO_3$ in 1000 cc. of water and wash as in the case of cotton for 1 hour at 50° C.

(3) FASTNESS TO PERSPIRATION.—Dissolve 50 grams of 50% acetic acid and 100 grams of NaCl in a liter of water. Immerse a portion of the sample in this solution for 15 minutes, let dry and repeat the operation twice. Compare the final dry piece with the original and note any change.

(4) FASTNESS TO MUD SPOTS.—Splash a sample of material with street mud, let dry, brush off the mud, and note the effect.

(5) HOT IRONING TEST.—Iron with a hot iron and note if heat changes the color. This shows the sensitiveness of colors to heat and in many cases, especially with light shades, colors will be found to change to a considerable extent. Most of them assume their original shade on cooling, but in some cases the change is permanent. The test is also of value on certain classes of fabrics, such for instance as Bolivia cloths, where hot ironing, especially in the presence of moisture, tends to destroy the surface finish of the fabric.

In the case of heavily weighted silks, continued hot ironing will have a tendency not only to change the shade of some of the

* This is generally considered equivalent to about 1 week of bright sunlight.

colors, but to cause the material to deteriorate and, in some instances, to crack badly.

Hosiery.—In hosiery analysis the terms "wales" and "courses" are used and correspond to warp and filling, respectively, in woven fabrics. The term "reinforcing thread," used in toe and heel, applies to an extra thread twisted in to reinforce and give additional strength. The weight is reported in ounces per dozen pairs.

FIBERS IN CLOTH AND YARNS

General.—The following method gives the procedure to be used in analyzing a complex mixture of textile fibers. It is seldom that more than 2 fibers are found in the same fabric, and where the fibers are known, as for instance in a wool-cotton mixture, the procedure can be very much shortened.

Moisture.—Weigh 2–5 grams of the sample in a glass-stoppered weighing bottle and dry at 100–110° C. to constant weight. Report the loss as Moisture.

Sizing Materials, etc.—Boil the dry material from the moisture determination thoroughly in very dil. HCl. The acid solution should not be over 1% in strength and care must be taken not to disintegrate the fibers. If the fibers are much weakened or disintegrated, repeat, using weaker acid. Repeat the boiling with fresh portions of acid until no residue is found upon evaporating a few drops of the liquid on a watch glass. This removes mineral loading matter soluble in HCl, finishing materials, and more or less dyestuff, as well as other materials soluble in water. Next extract with alcohol, and finally with ether, until all soluble material is removed. Dry and weigh. This gives the weight of anhydrous fibers, together with any mineral matter not soluble in HCl. Divide immediately into 2 parts, weighing each. Ash 1 portion. This will give the natural insoluble ash of the fibers (which is generally negligible) and any insoluble loading materials, such as certain mordants and tin salts. Calculate the weight to percentage of the original material.

Silk.—Heat to boiling about 60 cc. of basic $ZnCl_2$ solution,* and immerse in it the second portion of the above extracted sam-

* The zinc chloride solution is made as follows: Add an excess of Zn metal to conc. HCl and let stand 24 hours. Filter through glass wool and slightly acidify with HCl.

ple. Remove the flame, stir the sample thoroughly for about 1 minute, and again bring to boiling. Transfer immediately to a previously weighed Gooch crucible, using the insoluble fibers (cotton and wool) as a mat for the crucible. Remove the insoluble fibers to a beaker containing cold, dil. HCl (5%). Thoroughly wash in the beaker by agitation and again filter. Repeat the process several times to remove all $ZnCl_2$, using a weaker acid solution at each subsequent washing. Finally remove to the crucible and finish the washing with several portions of hot water until free from Cl. Dry at 100–105° C., and weigh. The loss in weight represents silk (and in certain cases a portion of the sizing material). If the material is pure natural silk, no residue is left at this point of the analysis.

NOTE.—This treatment also removes artificial silk (rayon).

Wool.—Treat the above residue with about 100 cc. of a solution of approximately 5% KOH and boil gently for 10–15 minutes. Pour into 500 cc. of cold water, let stand until the fibers have settled, and decant carefully the supernatant liquor, taking care to avoid loss of any fibers. Filter through a weighed Gooch crucible and wash thoroughly with boiling water. Moisten with a few cc. of dil. acetic acid and again wash with hot water, and finally with about 10 cc. of alcohol. Dry and weigh. The loss in weight by the KOH treatment represents wool.

Cotton, etc.—The residue in the crucible at this stage is cotton, or vegetable fibers (wood fiber, jute, linen and similar material). Ignite and weigh. The loss represents the various fibers, the nature and approximate proportions of which must be determined microscopically on another portion. The residue in the crucible may consist of asbestos, mineral wool, etc., and should be examined qualitatively and microscopically (see Calculation of Results).

Cotton-wool Mixtures.—In the case of fabrics consisting only of cotton and wool, determine the moisture as above described and remove sizing materials, if necessary, by boiling with 1% HCl solution. Wash out the acid and dry at 105° C. to get the total weight of fibers. If the material is known to contain a considerable amount of wool (at least 15–20%), use Method *A* described below; if the amount of wool is small, use Method *B*.

As a preliminary test to determine qualitatively whether the sample contains a large or a small amount of wool, make the following dyeing test: Weigh out a piece of the goods and dye it in a bath containing 3% of indigo carmine and 2% of acetic acid, both percentages based on the weight of the goods. Dye at boiling temperature for about 15 minutes, working the goods thoroughly in the bath. The cotton will take a pale blue color and the wool will dye a much deeper blue. By examining the dyed cloth under a hand glass a good approximation of the amount of wool present may be obtained.

METHOD *A* (FOR GOODS HIGH IN WOOL).—Boil a weighed amount of the sample (from which sizing has been removed, if necessary) for 15–20 minutes with 5% KOH solution and proceed as directed previously under Wool, weighing the final residue of cotton.

METHOD *B* (FOR GOODS LOW IN WOOL).—Place a known weight of the sample in a considerable volume of a solution made by mixing 80 cc. of conc. H_2SO_4 and 25 cc. of water. The mixture must be cooled to room temperature before adding the sample. Work the sample in this mixture for about 15 minutes, removing it from time to time to another beaker and washing with a stream of water to remove the slimy product formed by the action of H_2SO_4 on the cotton. Finally filter the residue on a weighed Gooch crucible, wash with water until *entirely* free from acid, dry in the oven at 100° C. and weigh the residue, which in this case is the wool.

Calculation of Results.—About 3.5% of cotton* is soluble in the KOH solution. To obtain the true weight of bone-dry cotton, therefore, divide the actual weight of cotton by 0.965 and subtract the difference between the original and the corrected cotton figures from the wool as calculated by loss. Calculate the percentage of the various fibers on the bone-dry basis.

As the natural moisture of cotton fiber is different from that of wool, wherever the fabric has a cotton thread in one direction and wool in the other the threads should be separated and the moisture determined on the cotton and wool separately. In cases where wool and cotton are twisted together, however, this is not usually possible. The normal regain of wool is assumed

* See notes (1) and (2).

to be 14%. For silk the regain allowed should be 11% and for cotton and vegetable fibers 6.5%. (For cellulose acetate rayon use 6.5%, and for all other rayon varieties 11.5%.) Where it is not possible to determine the moisture of the different fibers, the air-dry percentage should be figured by dividing the percentage of wool, cotton (vegetable fiber), and silk by 0.877,* 0.939 and 0.90, respectively. If the sum then exceeds 100% (showing that the fabric was below normal moisture), correct these figures by multiplying each percentage by $\frac{100}{A}$ where A is the sum total. If the sum of the air-dry corrected figures for wool, cotton, and silk, together with the sizing, is less than 100%, the difference (in the absence of mineral filler) may be reported as excess moisture.

EXAMPLE:

Preliminary analysis:

	Per cent
Moisture (loss at 100° C.)	5.74
Sizing, etc. (loss to HCl)	3.28
Fibers (by difference)	90.98
	100.00

Analysis of bone-dry fibers:

	Per cent of dry fibers	Per cent of original
Silk (loss to basic $ZnCl_2$)	22.10	20.11
Wool (loss to KOH)	30.64	27.88
Cotton (residue)	47.26	42.99
Total	100.00	90.98
Cotton (corrected, $42.99 \div 0.965$)		44.55
Wool (corrected, $27.88 - 1.56$)		26.32

Air-dry analysis:

	Per cent
Silk ($20.11 \div 0.90$)	22.34
Wool ($26.32 \div 0.877$)	30.02
Cotton ($44.55 \div 0.939$)	47.44
Sizing, etc	3.28
Total	103.08

* See note (3).

Final corrected analysis $\left(\text{air-dry analysis figures multiplied by } \frac{100}{103.08}\right)$:

	Per cent
Silk	21.7
Wool	29.1
Cotton	46.0
Sizing, etc	3.2
	100.0

NOTES.—(1) The figure of 3.5% for the solubility of cotton in KOH solution is necessarily approximate. The actual solubility depends upon the treatment the cotton has received, whether the goods have been bleached or are "in the grey," etc. Where possible, in order to get accurate results, the actual loss should be determined on the cotton which was used in making the goods.

(2) If the H_2SO_4 method instead of the KOH method is used, the bone-dry *wool* is weighed directly and no solubility correction is made on either wool or cotton.

(3) A regain of 14% means that 100 pounds of bone-dry fiber will regain 14 pounds of water when it comes back to normal moisture conditions. 14 pounds of water in 114 pounds of the moist material is equivalent to 12.3% of moisture.

Distinction between Natural and Artificial Silks.—The trade name Rayon has now been adopted for all classes of artificial silk. The principal varieties are:

(1) *Pyroxylin Silk* (*Chardonnet Silk**): made from a solution of nitrated cellulose in a mixture of alcohol and ether, the cellulose being usually afterwards denitrated with dil. HNO_3, $FeCl_3$ and $(NH_4)_2HPO_4$.

(2) *Cuprammonium Silk* (*Pauly Silk*): made from a solution of cellulose in ammoniacal copper solution (or sometimes ammoniacal chloride of zinc).

(3) *Viscose Silk;* made from a solution of alkaline cellulose xanthate prepared by the action of NaOH and CS_2 on mercerized cellulose.

(4) *Gelatin Silk;* made from gelatin filaments rendered insoluble by treating with formaldehyde.

(5) *Acetate Silk* (*Celestron Silk, Lustron Silk*): made from cellulose acetate.

* *Lehner Silk* is also a pyroxylin silk made by a process somewhat different from that of Chardonnet.

A cold solution of chromic acid dissolves all rayons, whereas real silk dissolves but slowly and cotton and other vegetable fibers are unaffected. KOH solution does not dissolve collodion or cellulose silks, but in a boiling solution gelatin silk and real silk are soluble. Schweitzer's reagent dissolves collodion and cellulose silks, as well as natural silk, whereas gelatin silk is insoluble and stains the liquid bright violet. Loew's reagent dissolves real silk immediately at 80° C. It will dissolve Tussah and gelatin silk when boiled for 1 minute; other artificial silks are not affected. The best solution for separating real silk from wool, cotton, and rayon is Loew's reagent.

The differentiation between the 3 most common varieties of artificial silks, namely, Pyroxylin, Cuprammonium and Viscose silks, can be quickly made with 2 reagents, Fehling's solution and zinc chloride-iodine solution, as follows:

Heat 0.2 gram of the silk with 2 cc. of Fehling's solution on the water bath for 10 minutes in a test-tube and then fill the test-tube with water. Pyroxylin rayon produces a green color, whereas the other two give a clear blue. Furthermore, on the threads of the pyroxylin rayon there will be noticeable a yellowish precipitate of cuprous oxide or hydroxide. The reaction depends upon the different reducing powers of the rayons. Only in the case of the pyroxylin rayon (nitrocellulose) is the reducing power appreciably increased.

To distinguish further between cuprammonium and viscose rayons, cover equal weights of the silks in a test-tube with zinc chloride-iodine solution and after a few seconds pour off the excess of the reagent. Then fill the test-tube with water, pour the water off and repeat this washing process until the water is only light yellow or colorless. Cuprammonium rayon is only weakly colored under these conditions and loses the brown shade very quickly when washed, whereas viscose rayon is colored a bluish-green and retains the color a longer time.

Cellulose acetate rayon is soluble in a mixture of 5 parts of chloroform and 2 parts of denatured alcohol by volume. It also is readily soluble in pure acetone in concentrations of not over 1%. It burns rather slowly and hardens at once into a brittle substance globular in appearance. As a confirmatory test it may be saponi-

fied with KOH, forming potassium acetate, which in turn will yield acetic acid when treated with H_2SO_4.

Pyroxylin rayon which has *not* been denitrated can also be saponified with KOH, forming KNO_3 which may be identified by the common qualitative test for nitrates. The denitrated variety contains traces of N and small amounts of oxycellulose. The N may be detected by moistening on a glass plate with a solution of diphenylamine in conc. H_2SO_4. Pyroxylin rayon gives a dark blue color; cuprammonium and viscose are not colored. The oxycellulose reduces Fehling's solution as above described.

It is advisable in making the above identity tests to run comparision tests with artifiical silks of known origin.

Reagents.—The different reagents are made up as follows:

(*a*) *Schweitzer's Reagent.*—Dissolve 5 grams of copper sulfate crystals in 100 cc. of boiling water, add NaOH solution to complete precipitation, wash the precipitate thoroughly, and then dissolve in the least quantity of conc. NH_4OH. This should give a deep blue solution.

(*b*) *Loew's Reagent.*—Dissolve 16 grams of copper sulfate in 150 cc. of water and add 10 grams of glycerol. Then add carefully a solution of NaOH until the precipitate which at first forms is just redissolved.

(*c*) *Fehling's Solution.*—The Fehling's solution is made by mixing just before use equal volumes of the Soxhlet modifications of Fehling's copper solution, and Fehling's alkaline tartrate solution, the formulas of which are given on page 3.

(*d*) *Zinc Chloride-Iodine Solution.*—Dissolve 2 grams of KI and 0.1 gram of iodine in 5 cc. of water. Add to this a solution of 20 grams of $ZnCl_2$ in 10 cc. of water. Let settle and use the clear solution.

(*e*) *Diphenylamine.*—Dissolve 1 gram in 100 cc. of conc. H_2SO_4.

Selective Dyeing Tests.—It is difficult and oftentimes impossible by chemical analysis to detect the presence of a small amount of one fiber when mixed with a large amount of other fibers. In such cases the method of selective dyeing often gives valuable information. The principle of this method is that certain dyes have an affinity for one fiber and not for another. Following is a list of the more common mixtures of fibers and the

method of applying selective dyes to them. If the fibers have already been dyed when received, the dye should be stripped off before making the test. This can usually be accomplished by boiling in a 3% solution of sodium hydrosulfite. After the color has been stripped, wash the material thoroughly with water to remove the stripping agent. All percentages given below are based on the weight of the goods dyed.

Cellulose Acetate and Viscose Rayons.—Dye a portion of the sample in a bath containing 3% of NaCl and 3% of a direct cotton color. (A suitable color is Newport Direct Sky-blue FF.) The viscose will be dyed a full shade of blue and the cellulose acetate will remain undyed. Any undyed fibers may be removed and treated with a mixture of 5 parts of $CHCl_3$ and 2 parts of denatured alcohol by volume. Cellulose acetate rayon is soluble in this mixture.

Wool and Cotton.—Dye a piece of the goods at boiling temperature for $\frac{1}{2}$ hour in a dye-bath containing 1% of indigo carmine and 2% of acetic acid. Work the goods in the bath thoroughly while dyeing, then remove and wash well with water. The cotton will be left undyed, whereas the wool will be dyed a full shade of blue. By drying the dyed material and examining under a magnifying glass, the percentage of wool or cotton may be estimated.

Silk and Wool.—Dye a piece of the goods for $\frac{3}{4}$ of an hour just under boiling temperature in a bath containing 2% of National Superchrome Red B (National Aniline and Chemical Company) and 1.5% of acetic acid. Then add 2% of $K_2Cr_2O_7$ and boil for $\frac{1}{2}$ hour. Remove from the bath and wash thoroughly. The silk will be undyed and the wool will be dyed a full red shade.

Wool and Rayon.—Follow the same direction as for Wool and Cotton. The rayon will be left undyed and the wool will be dyed a full blue shade.

Cotton and Natural Silk.—Follow the directions under Wool and Cotton. The silk will be dyed a full shade while the cotton is left undyed.

References: J. M. Mathews: "The Textile Fibers;" *Wochbl. Papierfabr.*, Nov. 30, 1907; Worden: "Nitrocellulose Industry," **1**, 560; American Society for Testing Materials, Standards.

CHEMICAL TESTS OF ROPES AND TWINES

General.—The chemical tests usually desired on ropes and twines are:

(1) Moisture.

(2) Ether extract, to show the amount of oil or tar.

(3) Water extract, to show whether the material has been treated with any chemicals, such as $CaCl_2$ solution.

(4) Ash.

Sampling.—It is very important to get a representative sample. On twine and small rope, obtain samples by cutting pieces 2 or 3 inches long from sufficient portions to represent the whole sample. If the twine is wound on a spindle or card, discard the abnormally dry outside layer and take samples from the interior. On large ropes and cables, unstrand the material and take portions not only from each strand but also representative of the outside and inside of the twists in each strand. In making the analysis it will save calculation if an even number of grams is weighed out.

Ether Extract.—Weigh out 10 grams and extract (preferably in a straight extractor) with ether for 10–16 hours. Dry the extract to constant weight at not over 100° C.

Moisture.—Dry the residue from the ether extract to constant weight at 100° C. and calculate the total percentage loss from the original weight. This loss will be moisture plus ether extract. Subtract from this the ether extract to obtain the moisture.

Water Extract.—Place the dried residue from the ether extract in a beaker and heat to boiling with water. Decant the water through a filter, catching the filtrate in a liter volumetric flask. Drain off as much water as possible and again heat to boiling with a fresh portion of water. Repeat this five to eight times, or until the filtrate is colorless, using about 100 cc. of water each time. Make up to the mark with water and pipette out an aliquot of 200 cc. (representing 2 grams of the original). Evaporate to dryness on the steam bath in a weighed platinum dish and then dry to constant weight in the oven at 100° C. Cool in a desiccator and weigh. Report the result as Total Water-soluble Matter.

Ignite the above residue at not over dull red heat until all carbon is burnt off. Cool in a desiccator and weigh. Report the result as Water-soluble Mineral Matter.

NOTES.—(1) If merely the total water-soluble is desired, the residual fiber after extracting may be dried to constant weight at 100° C. and the loss to water reported as Water-soluble Matter.

(2) In case the ash fuses, let it cool, dissolve in hot water, filter through a quantitative filter, ignite the filter paper in the weighed platinum dish, then add the filtrate, evaporate to dryness, ignite gently, cool in a desiccator, and weigh.

Ash of Fiber.—If the residual fiber from the water extract has been dried to constant weight, weigh out 2 grams quickly and ignite in a weighed platinum crucible to a white ash; cool in a desiccator and weigh. Calculate the ash to the original basis.

If the residual fiber from the water extract has not been dried, drive off the bulk of water on the steam bath and ignite in a weighed platinum crucible, in small portions at a time, taking care to avoid drafts which would blow any of the light ash from the crucible. (For the same reason the fiber should not be allowed to take fire and burn but should be smoked down to a char before raising the heat.) In this case, in calculating the percentage, use the original weight of 10 grams.

NOTE.—The ash thus obtained is the natural ash of the fiber. The total ash would be the sum of this ash and the water-soluble mineral matter.

Fiber.—The fiber is obtained "by difference." Add together the percentages of ether extract, moisture, water soluble and ash of the fiber, and subtract the sum from 100%.

DIFFERENTIATION OF ROPE AND CORDAGE FIBERS

General.—In this country ropes are generally made from the following fibers:

(1) *Manila,* fine and coarse.

(2) *Sisal.*

- (*a*) *Mexican.* This is the most common and cheapest.
- (*b*) *East African,* which is now out of the market.
- (*c*) *Java.*
- (*d*) *Bahama.*

(3) *New Zealand Flax.* This is not a true flax.

(4) *Mauritius.*

(5) *Tampico* or *Istle.*

(6) *Flax, Hemp* and *Jute:* used for twines but not much for rope.

Abroad hemp is used mixed with other fibers. An experienced eye can distinguish between manila and sisal but not, generally speaking, between sisal from different sources.

New Zealand flax may generally be distinguished under the microscope by the presence of fibrillæ which give it a ragged appearance.

Istle or Tampico is distinct because the fiber is of a horny character and is nearly round like a horse hair. The length is usually under 2 feet, much shorter than other rope fibers.

Distinction between Sisal and Manila.—For distinguishing between *sisal* and *manila,* use the Swett color reaction* with bleach followed by NH_4OH. This test was developed in this laboratory and is as follows: Submerge the suspended fibers in a solution of chloride of lime (bleaching powder) made distinctly acid with acetic acid. This solution should contain 3–6% of available chlorine. After the fibers have soaked for 5 minutes, remove, rinse with water and immerse in dil. NH_4OH (1 : 1). Examine the resulting color at once, as after 5 minutes it is likely to change. Manila gives an umber-brown, hemp a faint pink, and most of the other fibers a cherry-red. The umber-brown color appears to be characteristic of manila.

For applying this test to rope, it is advisable to remove the oil with ether previous to staining.

Microscopic Examination.—To prepare a slide from a rope or yarn for microscopic examination, take a strand and remove the oil with ether. Then boil with NaOH solution (about 5%) for 2 or 3 minutes, rinse, stain if desirable, and finally rinse again. While the fibers are still damp and relatively soft, trim the end with a razor or a sharp knife. Then, resting the bundle on a piece of wood, cut the end across. The bundle usually sticks together as a unit. The length of the sections need not be over 1 mm. Separate these cut ends on a slide, add a drop of 50% glycerol and press with the flat side of a knife blade to break up the fiber bundles. Finally cover with a cover-glass and examine under the microscope, using 100–300 diameters magnification. If spiral vessels are seen, it means that the sample contains some fiber other than manila.

* *J. Ind. Eng. Chem.*, **10,** 227 (1918).

ASBESTOS COTTON TWINE

General.—In a twine consisting of asbestos and cotton, a determination of the loss on ignition will give an approximation of the amount of cotton present, provided the loss on ignition of the asbestos itself can be ascertained. As this is not generally possible, however, and since the loss on ignition of asbestos from different sources varies widely, it is generally necessary to determine the cotton by dissolving it out with Schweitzer's reagent or by determining the amount of carbon and calculating the cotton from the carbon. Results are usually reported on the moisture-free basis.

Moisture.—Determine the moisture on a separate sample by drying 1 gram to constant weight at 105° C. in a weighing bottle. As the material is hygroscopic, it must be weighed with the weighing bottle stoppered.

Loss on Ignition.—The dried sample from the moisture determination may be used for the loss on ignition, which is conducted in the usual way in a platinum crucible.

Cotton.—By Schweitzer's Reagent.—Weigh out 1 gram of the twine* and treat in the cold with Schweitzer's reagent, using at least 100 cc. of the reagent per gram of the twine. Let stand for several hours, preferably overnight; dilute to several times its volume with water and decant through linen cloth on a Büchner funnel. (The best linen for this purpose is that used in the determination of crude fiber.)

Wash with warm water, and then with cold, to remove the copper clinging to the asbestos fibers. Remove the residue from the linen and again digest with Schweitzer's reagent, washing as before. Dry the fibers at 100° C. in a tared weighing bottle, cool in a desiccator and weigh. Repeat the process of digestion, washing and weighing until the twine ceases to lose weight upon further treatment with the reagent. The loss to Schweitzer's reagent is the cotton plus the free moisture, which is determined on a separate portion and subtracted.

Notes. – (1) *Schweitzer's Reagent.*—Dissolve 25 grams of copper sulfate crystals in 500 cc. of water and precipitate the Cu by adding a slight excess

* Many asbestos cotton twines are reinforced with a brass or copper wire. This wire should be removed before making the analysis and the results reported on the twine itself, unless otherwise instructed.

of 10% NaOH solution. Wash the precipitate to remove the excess of caustic and dissolve in an excess of conc. NH_4OH. The precipitated $Cu(OH)_2$ should be light blue in color and the final solution in ammonia dark blue.

The reagent should always be tested with absorbent cotton to see that it works properly. The directions for making up should be followed exactly and the final solution should dissolve cotton completely in the cold. The solution readily decomposes and should be made up rapidly, and only in small quantities as needed.

(2) If the fibers appear blue after washing with cold water, the last traces of Cu may be removed by washing with an extremely dilute solution of acetic acid, followed by a further washing with water, before drying.

(3) This method is based on analyses carried out in this laboratory.

By Carbon Determination.—The Underwriters' Laboratories in their specification for standard heater cord require that "asbestos coverings, after extraction to remove finishing compounds and impregnating compounds, must have a carbon content of not over 10%." This is based on the assumption that cotton is practically pure cellulose, containing 44.4% of C, and an asbestos covering which contains 20% of cotton by weight, and no other material which will appear as C in the method of analysis, will show about 9–10% of C under the test described below.

Before determining the C, make certain that the sample is free from oil or impregnating compound. In case of doubt on this point, extract it thoroughly with $CHCl_3$ or some other reagent in which the compound is soluble. Then weigh 1 gram into a small porcelain or alundum boat and determine the C in an electric combustion furnace as described under Carbon in Steel (p. 134). In this case, however, it is preferable to have the temperature about 870° C.

If the percentage of cotton is desired, divide the percentage of C by 0.444.

Notes.—(1) A blank determination should be conducted in a manner exactly similar to the test for C, except that the sample of asbestos twine is omitted. The blank should be very small and should be subtracted from the weight of CO_2 found.

(2) The C thus found will include the C of any other organic matter besides cotton, and also, if any $CaCO_3$ is present, it will give up its CO_2. The Underwriters' specifications, however, require that the asbestos must not be loaded or weighted and also place a maximum limit of 10% on the C as above determined.

CHAPTER X

ANALYSIS OF FOODS

COLORING MATTER IN FOODS

General.—The following procedures are from the tentative methods of the Association of Official Agricultural Chemists, published in its "Methods of Analysis" (1925), page 139.

Coloring matters may be divided into 3 classes: (1) Insoluble Pigments, (2) Soluble Dyes and their Lakes, and (3) Natural Coloring Matters.

Pigments

The insoluble pigments, ultramarine, lampblack, etc., are most commonly used as facings and may be separated by washing the sample with water and letting the washings settle. The particles of coloring matter can be identified by microscopic examination and by chemical tests of the residue or purified coloring matter.* Most of the common pigments other than lakes, such as the yellow, brown, and red ochers and umbers, are derivatives of the heavy metals and contain Fe, Mn, etc. Others, such as various green and blue compounds, including certain green chlorophyll derivatives, may contain Cu.

Soluble Dyes and Their Lakes

(Wool Dyeing Test)

Water-soluble Coal-tar Dyes.—(*a*) *Wines, fruit juices, distilled liquors, flavoring extracts, vinegars, beers, syrups, non-alcoholic beverages and similar products.*—Dilute 20–200 cc. of the sample with 1–3 volumes of water, neutralize with dil. NH_4OH (1:9) if necessary, and boil, or heat on the steam bath, with a small piece of white woolen cloth (nun's veiling). When the mixture contains much alcohol, heat until most of the alcohol has been

* See also Schultz: "Farbenstofftabellen," 5th German ed., 1914.

removed; in other cases, take out the wool after 5–15 minutes and rinse with water. Then treat the liquid with 3–4 drops of conc. HCl for each 100 cc. of solution and warm again for 10–20 minutes with a clean piece of wool. The basic dyes go on the fiber best from neutral or faintly ammoniacal solutions and, if present, will appear on the first piece of wool. Acid colors dye from neutral solutions, but more readily from those containing free acid. If the wool takes up any considerable amount of coloring matter in either case, the presence of coal-tar dyes is indicated. The lichen colors (Archil, Cudbear, Litmus) go readily on wool, however, and many other natural colors, such as Turmeric, will dye the fiber, if present in considerable amount. On the other hand, a few coal-tar dyes, especially Auramine O and Naphthol Green B, are quite unstable and, if present in small amounts, may give no distinct dyeing.

Acid dyes are much more frequently used than basic dyes and in most cases may be removed from wool without much decomposition by "stripping" the latter with dil. NH_4OH. By the action of the alkali many natural colors are destroyed, while others remain for the most part on the fiber. If the behavior with wool in neutral and acid solutions indicates the presence of acid dyes, rinse the colored cloth thoroughly with water, cover with dil. NH_4OH (1:9) in a casserole, boil for a few minutes, remove the cloth and squeeze out the adhering liquid. Boil the ammoniacal solution to remove the excess of NH_3, drop in a piece of clean, wet wool, make distinctly but not strongly acid with dil. HCl (1:9) and boil again. If acid coal-tar dyes are present, they will usually give a fairly clean, bright dyeing on the second piece of wool. A further purification may be carried out by repeating the stripping and redyeing, though this is generally accompanied by corresponding loss of dye.

(*b*) *Candies and similar colored sugar products.*—Dissolve about 20 grams of the sample in 100 cc. of water and treat the solution as directed under (*a*). When the coloring matter is on the surface of the candy, pour off the solution before the colorless inner portion has dissolved.

(*c*) *Jams and jellies.*—Boil a mixture of 10–20 grams of the sample and 100 cc. of water with wool in neutral and also in acid solution as directed under (*a*). For thick jams it is usually

better, though less easy, to first extract the coloring substances by treating the product as directed below under (*d*).

(*d*) *Canned and preserved fruits and vegetables, sausage casings, smoked fish, coffee, spices, etc.*—Macerate 20–200 grams of the sample with 4–5 times its weight of 80% alcohol. After standing a few hours, pour off the solvent as completely as possible and repeat the extraction, using 70% alcohol containing about 1% of NH_4OH. (1) Examine separately the filtered alcoholic extracts as directed under (*a*); or, (2) boil the ammoniacal solution until practically neutral, complete the neutralization with acetic acid, add the neutral 80% alcohol extract, continue the evaporation until most of the alcohol is removed, and boil with wool as directed under (*a*).

(*e*) *Cocoa and chocolate products.*—Treat cocoa as directed under (*d*). The alcoholic extract will contain a large amount of natural coloring matter and several dyeings and strippings may be necessary to remove this in order to show the presence of coal-tar dyes.

Chocolate may be treated similarly but the following procedure is preferable: Wash 20–200 grams of the well-divided sample with gasoline on a filter until most of the fat has been removed; if the gasoline is colored, reserve for the examination of oil-soluble dyes as directed below under Oil-soluble Coal-tar Dyes. Remove most of the adherent solvent from the residue by evaporation or pressure between layers of absorbent paper and digest with alcohol as directed under (*d*).

Coal-tar dyes may also be detected in chocolate and cocoa products by mixing directly with three to four times their weight of hot water and immediately boiling the magma with wool, as directed under (*a*). Because of the presence of large amounts of fatty and protein materials, this method is not very satisfactory.

(*f*) *Cereal products.*—Proceed as directed under (*d*), in most cases working with a large amount of the sample, 200–300 grams, and a relatively smaller amount of alcohol. Where tests are to be made only for the acid dyes, the extraction with neutral 80% alcohol may be omitted advantageously.

Oil-soluble Coal-tar Dyes.—Prepare an alcoholic solution of the oil-soluble dye by one of the following methods, which

are to be applied to the oil or fat obtained by extraction with ether or gasoline, if the nature of the substance requires it:

(*a*) Shake the oil or melted fat with an equal volume of 90% alcohol and wash the alcoholic extract with several portions of gasoline to free the coloring matter from foreign fats. The alcohol after separation will contain Aniline Yellow, Butter Yellow, Aminoazotoluene, Auramine, etc., if present.

(*b*) Saponify 20–200 grams of the oil or fat with 0.5 N alcoholic KOH and, after removal of most of the alcohol on the steam bath, extract the soap with ether or gasoline. Most of the common dyes are removed by this treatment, though the digestion with strong alkali may cause some decomposition and make the extraction rather troublesome.

(*c*) Dilute 20–200 grams of the oil or melted fat with 1–2 volumes of gasoline and shake out successively with 2–4% KOH or NaOH solution, dil. HCl (1:2), and phosphoric-sulfuric acid mixture, prepared by mixing 85% H_3PO_4 with about 10–20% by volume of conc. H_2SO_4.

The dil. alkali extracts Sudan G and Annatto. The dil. HCl extracts Aniline Yellow (7)*, Aminoazotoluene, and Butter Yellow (16), the first two forming orange-red, the latter cherry-red solutions in this solvent. The H_3PO_4 mixture is necessary for the extraction of Sudan I (11), Sudan II (49), and Sudan III (143), and the homologue of the last, Sudan IV. Benzeneazo-betanaphthylamine and homologues also come in this group, though they readily decompose in the strongly acid mixtures. The procedure is not very suitable in the presence of Auramine, but this dye is seldom found in oils. Neutralize the alkaline and the dil. HCl solutions; dilute the H_3PO_4 mixture and partially neutralize, cooling the liquid during this operation; and extract the dyes by shaking with ether or gasoline.

For the direct dyeing test use the alcoholic solution obtained as directed in (*a*). Evaporate to dryness the ether or gasoline solutions, obtained as directed in (*b*) and (*c*) and dissolve the residue in 10–20 cc. of 95% alcohol. Add some strands of white

* The numbers following the names of the dyes in parenthesis are the numbers by which that dye is designated in "A Systematic Survey of the Organic Coloring Matters," by A. Green, 1904, translated from Schultz and Julius.

silk and a little water and evaporate on the steam bath until the alcohol has been removed or until the dye is taken up by the silk. The dyeing test is sometimes unsatisfactory and in all cases a small portion of the alcoholic solution should be tested by treatment with an equal volume of conc. HCl and $SnCl_2$ solution, respectively. The common oil-soluble coal-tar dyes are rendered more red or blue by the acid and are decolorized by the reducing agent. Most of the natural coloring matters become slightly paler with the acid and are little changed by the $SnCl_2$ solution.

NOTE.—For the separation and identification of the permitted coal-tar colors, see Association of Official Agricultural Chemists: "Methods of Analysis" (1925).

NATURAL COLORING MATTERS

Chlorophyll.—The "brown phase reaction" may be useful for the characterization of chlorophyll, when this has not been previously treated with alkalies. Treat the green ether or petroleum-ether solution of the coloring matter with a small quantity of 10% solution of KOH in methyl alcohol. The color becomes brown, quickly returning to green.

Annatto.—Pour on a moistened filter an alkaline solution of the color obtained by shaking out the oil or melted and filtered fat with warm, dil. NaOH solution. If annatto is present, the filter paper will absorb the color, so that when washed with a gentle stream of water it will remain dyed a straw color. Dry the filter and add a drop of $SnCl_2$ solution. If the color turns pink, the presence of annatto is confirmed.

Tumeric.—Treat an aqueous or dil. alcoholic solution of the color with HCl until the shade just begins to appear slightly orange. Divide the mixture into 2 parts and add some boric acid powder or crystals to one portion. A marked reddening will be quickly apparent, best seen by comparison with the portion to which the H_3BO_3 has not been added. The test may also be made by dipping a piece of filter paper in the other portion of the alcoholic solution of the coloring matter, drying at 100° C., then moistening with a weak solution of H_3BO_3 to which a few drops of HCl have been added. On drying again, a cherry-red color will be developed.

Cochineal.—When the presence of cochineal is suspected, acidify the mixture with $\frac{1}{3}$ its volume of conc. HCl and shake

with amyl alcohol. Wash the amyl alcohol solution of the coloring matter two to four times with equal volumes of water to remove HCl, etc. Dilute the amyl alcohol with 1–2 volumes of gasoline and shake with a few small portions of water to remove the color. Divide the combined aqueous extracts into 2 portions. To the first add, drop by drop, 5% uranium acetate solution, shaking thoroughly after each addition. In the presence of cochineal a characteristic emerald-green color is produced. The green coloration with uranium salts is not developed in the presence of much free acid. Therefore, add a little sodium acetate before making this test, or a correspondingly large quantity of uranium acetate must be added. To the second portion add 1 or 2 drops of conc. NH_4OH; in the presence of cochineal, a violet coloration results. This, however, is not so characteristic as the first test since many fruit colors give almost identical reactions.

As cochineal lakes often contain tin, further examination for this metal should always be made when water-insoluble cochineal compounds seem to be present.

METALS IN FOODS

General.—The principal metals which are to be looked for in foods as objectionable are arsenic, tin, copper and zinc.

Arsenic.—Determine As by the Sanger-Black-Gutzeit Method as described on page 52.

Tin.—Gravimetric Method.—Weigh 50–100 grams of the sample (depending upon the amount of dry substance present and the relative ease with which the organic matter is oxidized) into an 800-cc. Kjeldahl flask and add 100 cc. of conc. HNO_3. Let stand overnight (this procedure being preferred if much fat or sugar is present) or place the flask on a wire gauze over a free flame and heat until the contents boil quietly. Add 25–50 cc. of conc. H_2SO_4 (depending upon the amount of dry substance present in the sample), and heat until white fumes are generated. Cool somewhat, then add 5–10 cc. of conc. HNO_3 and continue heating as before. Repeat the addition of HNO_3 until the solution remains clear after boiling off the HNO_3 and white fumes of SO_3 appear.

Add 200 cc. of water to the digested sample and pour into a 600-cc. beaker. Rinse out the Kjeldahl flask with 3 portions of

boiling water, making a total volume of about 400 cc. Cool and add conc. NH_4OH until just alkaline and then 5 cc. of conc. HCl or of dil. H_2SO_4 (1 : 3) for each 100 cc. of solution. Place the beaker covered on a hot plate, heat to about 95° C., and pass in a slow stream of H_2S for 1 hour. Digest on the hot plate at 95° C. for 1 hour and let stand 1–2 hours longer.

Filter the SnS_2 on a close-textured, 11-cm. filter and wash alternately with 3 portions each of wash solution (100 cc. of saturated ammonium acetate solution, 50 cc. of glacial acetic acid, and 850 cc. of water) and hot water. Digest the filter and precipitate in a 50-cc. beaker with 3 successive portions of 10–20 cc. of ammonium polysulfide, heat to boiling and filter through a 9-cm. filter each time. Wash the filter with hot water. Acidify the combined filtrate and washings with dil. acetic acid (1:9), digest on the hot plate for 1 hour, let stand overnight and filter through a double 11-cm. filter. Wash alternately with 2 portions each of the wash solution and hot water and dry thoroughly in a weighed porcelain crucible. Ignite over a Tirrill flame, very gently at first to burn off the paper and convert the SnS_2 to SnO_2. Then heat the crucible, partly covered, strongly with a large Meker burner. Stannic sulfide must be roasted gently to the oxide, which may be heated strongly without loss by volatilization. Weigh as SnO_2 and calculate to Sn.

Calculation.—$SnO_2 \times 0.7877 = Sn$.

Volumetric Method.—*Reagents.*—(*a*) Air-free Wash Solution.—Dissolve 20 grams of $NaHCO_3$ in 2 liters of boiled water and add 40 cc. of conc. HCl. This solution should be freshly prepared before use.

(*b*) 0.01 N Iodine.—Standardize the solution frequently against (*d*), adding asbestos and proceeding as described below under Determination, except to omit the precipitation with H_2S and the boiling with HCl and $KClO_3$. The tin solution used for standardization should contain about the same amount of Sn as in the sample under examination.

(*c*) 0.01 N Sodium Thiosulfate.

(*d*) Standard Tin Solution.—Dissolve 1 gram of Sn in about 500 cc. of conc. HCl and dilute to 1 liter with water. 1 cc. contains 1 milligram of tin.

(*e*) Sheet Aluminum.—Use sheet Al, about 30-gage, free from Sn.

Determination.—Proceed as directed under Gravimetric Method above to "Digest on the hot plate for 1 hour and let stand 1–2 hours longer." Then filter with suction upon an asbestos mat in a Gooch crucible with a detachable bottom. Wash the precipitate a few times and then transfer the detachable bottom, asbestos mat and precipitate to a 300-cc. Erlenmeyer flask. Remove all traces of the precipitate from the inside of the crucible by means of a jet of hot water and a policeman, using a minimum amount of water for washing.

Add 100 cc. of conc. HCl and 0.5 gram of $KClO_3$ to the flask. Boil for about 15 minutes, making about 4 more additions of smaller amounts of $KClO_3$ as Cl is boiled off. Wash the particles of $KClO_3$ down from the neck of the flask with water and finally boil to remove Cl. Then add about 1 gram of the sheet Al to dispel the last traces of Cl.

Fit a 2-hole rubber stopper to the flask. Through one hole pass a bulbed glass tube reaching nearly to the surface of the liquid. Attach this to a large CO_2 generator through a scrubber containing water. The CO_2 leaves the flask by a short-bulbed tube in the second hole of the stopper and terminating slightly below it. Connect this second glass tube by a rubber tube to a glass tube about 10 inches long which is immersed in a cylinder of water to a depth of about 8 inches. This gives a water-seal to the delivery tube and a pressure against which the current of CO_2 must work. It also restrains any strong flow of gas when not desired and permits a gas pressure in the Erlenmeyer flask.

After the flask is connected, raise the delivery tube nearly out of the water-seal, allowing a rapid flow of CO_2 for a few minutes to dispel air. Then lower the delivery tube into the water-seal, slightly raise the stopper, and quickly drop into the flask 1–2 grams of sheet Al, folded into a narrow strip and slightly bent to prevent it from striking directly on the bottom of the flask. After the Al has entirely dissolved, raise the tube in the water-seal, allowing the CO_2 to pass through rapidly; place the flask upon a hot plate and boil for a few minutes. Remove the flask from the heat and cool in ice water (or cold running water), still maintaining the flow of CO_2. Lower the delivery tube into the cylinder, disconnect the flask and place a glass plug in the rubber tube through which the CO_2 enters the flask. Wash the tubes,

rubber stopper, and sides of the flask with the air-free wash solution, add starch paste and titrate at once with the 0.01 N iodine.

If desired, the titration may be made by slightly raising the rubber stopper after cooling, and adding an excess of the 0.01 N iodine. Then disconnect the flask, wash the tubes, etc. with air-free wash solution, and titrate the excess of iodine with 0.01 N sodium thiosulfate. Calculate results to Sn.

Copper.—Destroy organic matter as directed above under the Gravimetric Method for Tin. Concentrate the H_2SO_4 residue by continued digestion to a volume of 10–15 cc.; cool, dilute with a little water and transfer to a 400-cc. beaker. Rinse the Kjeldahl flask with water, adding the rinsings to the contents of the beaker; dilute to about 200 cc. and boil to expel nitrous fumes. Cool, make slightly alkaline with conc. NH_4OH, and boil to expel the excess of NH_3. Add 5 cc. of conc. HCl for each 100 cc. of solution, heat to incipient boiling and saturate the solution with H_2S. Let stand on the steam bath for a few minutes until the sulfide flocculates, filter and wash the precipitate with H_2S water. Protect the precipitate from contact with the air as much as possible, use only H_2S water for washing, and carry out this operation without interruption. Reserve the filtrate for determination of Zn, if necessary.

Place the filter containing the CuS precipitate in a small flask, add 4–5 cc. of conc. H_2SO_4 and an equal amount of HNO_3 and heat until white fumes appear. Continue the oxidation, adding a little conc. HNO_3 from time to time, until the liquid remains colorless upon heating to the appearance of white fumes. Cool, dilute with about 30 cc. of water, add an excess of Br water and boil until all Br is expelled. Determine the Cu as follows:

Remove from the heat and add a slight excess (about 7 cc.) of conc. NH_4OH. Again boil until the excess of NH_3 is expelled, as shown by change of color and partial precipitation. Then add a slight excess of 80% acetic acid (3 or 4 cc.) and boil for a minute. Cool to room temperature and add 10 cc. of 30% KI solution. Titrate at once with 0.01 N thiosulfate solution until the brown tinge has become weak, then add sufficient starch indicator to produce a marked blue solution. Continue the titration cautiously until the color due to free iodine has entirely vanished. The blue color changes towards the end to a faint

lilac. If at this point the thio be added drop by drop and a little time allowed for complete reaction after each addition, there is no difficulty in determining the end-point within a single drop.

NOTE.—The 0.01 N thio must be standardized against pure Cu foil. First standardize a 0.1 N thiosulfate solution against portions of about 0.2 gram of pure Cu foil, accurately weighed. Dissolve the foil in a 250-cc. flask with 5 cc. of HNO_3 (1:1). Dilute to 50 cc., boil to expel red fumes, add 5 cc. of strong Br water, boil off all Br, remove from the heat, add a slight excess of conc. NH_4OH and proceed as previously described. Then pipette 100 cc. of the standardized 0.1 N thio and dilute it to 1000 cc. in a liter volumetric flask, using freshly boiled distilled water. This gives a 0.01 N solution having $\frac{1}{10}$ the Cu factor of the solution standardized.

Zinc.—Proceed as directed above under Copper to the point indicated by the sentence "Reserve the filtrate for the determination of Zn, if necessary." Boil the filtrate containing the Zn to expel H_2S and to reduce the volume to about 250–300 cc., add a drop of methyl orange and 5 grams of NH_4Cl and make alkaline with conc. NH_4OH. Add dil. HCl (1:9), drop by drop, until the reaction is faintly acid, then add 10–15 cc. of 50% sodium or ammonium acetate solution and pass in H_2S for a few minutes until precipitation is complete. Let the precipitate settle, filter and refilter if necessary until the filtrate is clear. Then wash the precipitate twice with H_2S water. Dissolve the precipitate on the filter with a little dil. HCl (1:3), wash the filter with water, boil the combined filtrate and washings to expel H_2S, cool and add a distinct excess of Br water. Then add 5 grams of NH_4Cl and NH_4OH until the color, caused by free Br, disappears. Add HCl (1:3), drop by drop, until the Br color just reappears, then add 10–15 cc. of 50% Na or NH_4 acetate solution and 0.5 cc. of 10% $FeCl_3$ solution, or enough to precipitate all the phosphates. Boil until all Fe is precipitated. Filter while hot and wash the precipitate with water containing a little Na acetate. Pass H_2S into the combined filtrate and washings until all the ZnS, which should be pure white, is precipitated; filter upon a Gooch crucible, previously ignited and weighed, and wash with H_2S water containing a little NH_4NO_3. Dry the crucible and contents in the oven, ignite at a bright red heat, cool and weigh as ZnO. Calculate to Zn.

CALCULATION.—$ZnO \times 0.8034 = Zn$.

REFERENCE.—Association of Official Agricultural Chemists: "Methods of Analysis" 171–176, (1925).

CRUDE FIBER

General.—The so-called "official" method for determination of crude fiber as directed by the *U. S. Dept of Agriculture, Bur. of Chem., Bull.* 107, page 56, is a long and tedious process. It has been adopted in principle as the tentative method of the Association of Official Agricultural Chemists. The procedure was somewhat modified by M. O. Sweeney (*Bull.* 137, p. 57), so that the time consumed is considerably shortened. It has been claimed, however, that for certain kinds of feed-stuffs, especially those rich in protein, the Sweeney method is not entirely satisfactory. This has, therefore, been further modified by Cornelia Kennedy [*J. Ind. Eng. Chem.*, **4**, 600 (1912)]. The three methods are given below, but, except for special cases, the Kennedy modification is the one to be employed in routine work.

Official Method.*—REAGENTS.—(*a*) *Sulfuric Acid Solution.*—Contains 1.25 grams of H_2SO_4 per 100 cc.

(*b*) *Sodium Hydroxide Solution.*—Contains 1.25 grams of NaOH per 100 cc., free, or nearly so, from Na_2CO_3.

The strength of these solutions must be accurately checked by titration.

(*c*) *Asbestos.*—First digest a quantity on the steam bath overnight (or at least 8 hours) with an approximately 5% NaOH solution and wash thoroughly with hot water; then digest for a similar length of time with dil. HCl (1:3) and again wash thoroughly with hot water; finally dry and ignite at bright red heat.

APPARATUS.—(*a*) *Water-jacketed Condenser.*—Use any suitable form that will maintain a constant volume of solution throughout the process of digestion.

(*b*) *Containers.*—The digestion flasks should be of such size and shape that the depth of solution will be between 1 and 1.5 inches. A 700–750-cc. Erlenmeyer flask is recommended.

(*c*) *Filtering Cloth.*—The filtering cloth should be of such a character that while filtration is rapid no appreciable amount of solid matter passes through. Either butcher's or dress linen

* Association of Official Agricultural Chemists: "Methods of Analysis" 117, (1925)

with about 45 threads per inch may be used, or No. 40 filtering cloth,* or its equivalent.

DETERMINATION.—Extract 2 grams of the dry material with ordinary ether, or use the residue from the ether extract determination and transfer the residue, together with about 0.5 gram of asbestos, to the flask. (Where the residue from the ether extract is used and the proper amount of asbestos has already been added, further addition is unnecessary.) Add 200 cc. of boiling H_2SO_4 solution (*a*) to the contents of the flask and place immediately over heat after connecting with the condenser. Bring the contents of the flask to boiling within 1 minute and continue the boiling briskly for exactly 30 minutes. Rotate the flask about every 5 minutes in order thoroughly to mix the charge, taking care to keep the sides of the flask above the solution free from the sample. A blast of air conducted into the flask will serve to reduce the frothing of the liquid. Remove the flask at the expiration of the 30 minutes, immediately filter through linen in a fluted funnel, and wash with boiling water until the washings are no longer acid.

Next wash the charge and adhering asbestos back into the flask with 200 cc. of boiling NaOH solution (*b*), using a wash bottle calibrated to deliver 200 cc. Bring the NaOH to boiling and keep at this temperature under a reflux condenser while in use. (The boiling NaOH is best transferred to the 200-cc. wash bottle by means of a bent tube through which the liquid is forced by blowing into a tube connected with the top of the condenser attached to the NaOH flask.) Then place the flask over the heat, connected with the reflux condenser, and boil for exactly 30 minutes. Time the boiling with the alkali so that the contents of the different flasks will reach the boiling point approximately 3 minutes apart. This provides sufficient time for filtration. At the end of 30 minutes remove the flask and immediately filter through a Gooch crucible, which has been prepared previously with a thin but close layer of ignited asbestos. If preferred, an alundum crucible may be used, or filtering cloth in a fluted funnel. If the cloth is used, thoroughly wash the residue with boiling water and then transfer to the Gooch crucible. Wash the con-

* Made by National Filter Cloth & Weaving Company, 57 Hope Street, Brooklyn, New York.

tents thoroughly with hot water and then with about 15 cc. of 95% alcohol.

Dry the crucible and contents to constant weight at 110° C. Cool in an efficient desiccator and weigh. Incinerate the contents of the crucible in an electric muffle or over a Meker burner at a dull red heat until the carbonaceous matter has been consumed (20 minutes is usually sufficient). Cool in a desiccator and weigh. Report the loss in weight as Crude Fiber.

Sweeney Modification.—Place 2 grams of the oil-free material in a wide-mouthed Erlenmeyer flask of liter size, inserting a small air condenser in the mouth of the flask to prevent concentration due to loss of steam. To the sample in the flask add 0.5 gram of prepared asbestos and 200 cc. of a boiling 1.25% solution of H_2SO_4, as in the Official Method. Heat to boiling and after gently boiling for 30 minutes treat as follows:

Neutralize with a 10% solution of NaOH, using a few drops of phenolphthalein as indicator. Approximately 25 cc. of NaOH solution are required. Add at once 200 cc. of a boiling solution of NaOH containing 2.656 grams of NaOH per 100 cc. This solution should be prepared as accurately as possible by titration. Continue the digestion at the boiling point for 30 minutes longer in the same manner as in the treatment with acid. Then filter the alkaline solution containing the fiber residue rapidly through a linen cloth and wash repeatedly with boiling water. Transfer the fiber residue and asbestos to a weighed platinum Gooch crucible and wash with alcohol and finally with ether. Dry at 110° C. to constant weight. Ignite the dried residue and again weigh. The loss in weight gives the weight of crude fiber.

Kennedy Modification.—Digest 2 grams of the fat-free sample, together with 0.5 gram of prepared asbestos, with 200 cc. of a 1.25% H_2SO_4 solution by boiling 30 minutes in a liter Erlenmeyer flask connected to an air condenser exactly as in the Sweeney Modification. Then add directly 200 cc. of a solution of NaOH containing 3.52 grams of NaOH per 100 cc., the solution being made of this exact strength by titration. Boil the whole for 30 minutes, filter through linen, and wash free from alkali with hot water. Then wash thoroughly with boiling 1.25% H_2SO_4 which will remove any material precipitated by the addition of the alkali. Wash free from acid. Transfer from the linen filter to a weighed

Gooch crucible, wash with alcohol, then with ether, and dry to constant weight at 110° C. Weigh the residue, ignite and reweigh. The loss indicates the amount of crude fiber.

SULFUR DIOXIDE IN FOODS

General.—Free sulfurous acid in the form of sulfur fumes is extensively employed to bleach molasses, disinfect wine casks, and to bleach and preserve dried fruits. The process is known as "sulfuring." The sulfurous acid salts most commonly employed as preservatives are the bisulfites of Na and of Ca. The normal sulfites (Na, K or NH_4) are most commonly used as preservatives in fruit juices, ketchup, fruit and vegetable pulp, wines, malt liquors, and meat products. They are frequently mixed with other antiseptics, such as salicylates and benzoates.

Determination.—The same methods are used for the qualitative detection of SO_2 as for its quantitative determination, except that in the former case weighed quantities need not be employed.

(*A*) Distillation Method.—This method is adapted to all food products whether solid or liquid.

Place 20–100 grams of the material in a 500-cc. flask, add water, if necessary, and 5 cc. of a 20% solution of H_3PO_4, and distill in a current of CO_2 into about 100 cc. of water containing a few drops of bromine, until 150 cc. have passed over. Have the end of the condenser dip below the surface of the liquid. If sulfides are present, as is true of decomposed meat products and possibly other foods, the steam from the distilling flask before entering the condenser should be passed through a flask containing 40 cc. of a 2% neutral solution of $CdCl_2$ or a 1% solution of $CuSO_4$. These solutions effectually remove the H_2S without retaining any appreciable amount of SO_2.

The method and apparatus may be simplified without material loss in accuracy by omitting the current of CO_2, adding 10 cc. of H_3PO_4 instead of 5 cc., and dropping into the distilling flask a piece of $NaHCO_3$, weighing not more than a gram, immediately before attaching the condenser.

When the distillation is finished, boil off the excess of Br, dilute to about 250 cc., add 1 cc. of conc. HCl, heat to boiling and add, drop by drop, while boiling, an excess of 10% $BaCl_2$ solution. Let stand overnight in a warm place, filter, wash with hot

water, ignite at a dull red heat and weigh as $BaSO_4$. Calculate to SO_2 and report as parts per million. Run a blank on the apparatus and reagents used and subtract any SO_2 found in the blank.

CALCULATION.—$BaSO_4 \times 0.2744 = SO_2$.

(*B*) DIRECT TITRATION METHOD.—This method is applicable to light-colored liquids such as white grape juice, wines, and similar products, but should not be used for other materials unless found by experiment to yield accurate results.

To 25 cc. of a N solution of NaOH or KOH in a 200-cc. flask, add 50 cc. of the sample; shake thoroughly and set aside for 15 minutes, with occasional shaking; and then add 10 cc. of dil. H_2SO_4 (1:3) and a little starch solution and titrate the mixture with 0.02 N iodine solution, introducing the latter quite rapidly, until a blue color is produced which persists for several minutes.

CALCULATION.—1 cc. 0.02 N iodine = 0.00064 gram SO_2.

REFERENCES.—Leach: "Food Inspection and Analysis," 840 (1913); Association of Official Agricultural Chemists: "Methods of Analysis," 135 (1925).

BENZOIC ACID IN FOODS

Preparation of Sample.—(*A*) GENERAL METHOD.—If solid or semisolid, grind the sample, and mix thoroughly. Transfer 150 cc. or 150 grams to a 500-cc. volumetric flask, add enough pulverized NaCl to saturate the water in the sample, render alkaline to litmus with 10% NaOH solution or milk of lime, and dilute to the mark with saturated salt solution. Shake well, let stand for at least 2 hours, with frequent shaking, and filter. If the sample contains large amounts of matter precipitable by salt solution, proceed as directed below under (4) Salted or Dried Fish. When alcohol is present, follow the method given under (3) Cider Containing Alcohol, etc. When large amounts of fats are present, add a few cc. of NaOH solution to the filtrate and extract with ether before proceeding as directed under the Quantitative Determination.

(*B*) SPECIAL METHODS.—(1) *Ketchup.*—To 150 grams of ketchup add 15 grams of pulverized NaCl. Transfer the mixture to a 500-cc. volumetric flask, rinsing with about 150 cc. of saturated NaCl solution. Make slightly alkaline to litmus with 10% NaOH solution and fill to the mark with saturated

salt solution. Let stand for at least 2 hours, shaking frequently. Squeeze through a heavy muslin bag and then filter through a large folded filter.

(2) *Jellies, Jams, Preserves, and Marmalades.*—Digest 150 grams of the sample in about 300 cc. of saturated salt solution. Add 15 grams of pulverized NaCl. Make alkaline to litmus with milk of lime. Transfer to a 500-cc. volumetric flask and dilute to the mark with saturated salt solution. Let stand for at least 2 hours, shaking frequently; centrifugalize if necessary, and filter through a large folded filter.

(3) *Cider Containing Alcohol, and Similar Products.*—Make 250 cc. of the sample alkaline to litmus with 10% NaOH solution and evaporate on the steam bath to about 100 cc. Transfer the sample to a 250-cc. volumetric flask, add 30 grams of pulverized NaCl and shake until dissolved. Dilute to the original volume, 250 cc., with saturated salt solution, let stand for at least 2 hours, shaking frequently, and filter through a folded filter.

(4) *Salted or Dried Fish.*—Wash 50 grams of the ground sample into a 500-cc. volumetric flask with water. Make slightly alkaline to litmus with 10% NaOH solution and dilute to the mark with water. Let stand for at least 2 hours, shaking frequently, and then filter. Pipette as large a portion of the filtrate as possible (at least 300 cc.) into a second 500-cc. flask. Add 30 grams of pulverized NaCl for each 100 cc. of solution. Shake until the salt has dissolved and dilute to the mark with saturated salt solution. Mix thoroughly and filter off the precipitated protein matter.

Qualitative Tests.—Extract benzoic acid as directed under Salicylic Acid, Ferric Chloride Test (p. 535) or Quantitative Determination (p. 536). If benzoic acid is present in considerable quantity, it will crystallize from the ether in shining leaflets having a characteristic odor on heating. Dissolve the residue in hot water, divide into 2 portions, and test as below.*

(*A*) Ferric Chloride Test.—Make the above solution alkaline with a few drops of conc. NH_4OH, expel the excess of NH_3 by evaporation, dissolve the residue in a few cc. of hot water, and

* The residue may also be purified by sublimation as directed under Salicylic Acid, Ferric Chloride Test and the melting point determined. Benzoic acid melts at 121° C.

add a few drops of a *neutral* 0.5% $FeCl_3$ solution. A brownish precipitate of ferric benzoate indicates the presence of benzoic acid.

(*B*) Modified Mohler Test.*—Add to the water solution, prepared as previously described, 1 or 2 drops of 10% NaOH solution and evaporate to dryness. To the residue add 5–10 drops of conc. H_2SO_4 and a small crystal of KNO_3. Heat for 10 minutes in a glycerol bath at 120–130° C. The temperature must not exceed 130° C. After cooling add 1 cc. of water and make distinctly ammoniacal. Boil to decompose any NH_4NO_2 which may have been formed. Cool and add a drop of fresh, colorless $(NH_4)_2S$ solution, wihout letting the layers mix. A red-brown ring indicates benzoic acid. On mixing, the color diffuses through the whole liquid and, on heating, finally changes to greenish-yellow. This differentiates benzoic acid from salicylic acid or cinnamic acid, which form colored compounds not destroyed by heating.

Quantitative Determination.—Pipette a convenient portion (100–200 cc.) of the filtrate, obtained under Preparation of Sample, into a separatory funnel. Neutralize to litmus with dil. HCl (1:3) and add 5 cc. in excess. In the case of salted fish a precipitation of protein matter usually occurs on acidifying, but this does not interfere with the extraction. Extract carefully with $CHCl_3$, using successively portions of 70, 50, 40, and 30 cc. To avoid an emulsion, shake cautiously each time. The $CHCl_3$ layer usually separates readily after standing a few minutes. If an emulsion forms, break it by stirring the $CHCl_3$ layer with a glass rod, by drawing it off into a second funnel and giving 1 or 2 sharp shakes from one end of the funnel to the other, or by centrifugalizing for a few moments. As this is a progressive extraction, draw off carefully as much of the clear $CHCl_3$ solution as possible after each extraction, but do not draw off any of the emulsion. If this latter precaution is taken, the $CHCl_3$ extract need not be washed.

Transfer the combined $CHCl_3$ extracts to a porcelain evaporating dish, rinse the container several times with a few cc. of $CHCl_3$, and evaporate to dryness at room temperature in a current of dried air.

* The presence of phenolphthalein interferes with this test.

The extract may also be transferred from the separatory funnel to a 300-cc. Erlenmeyer flask, rinsing the separatory funnel three times with 5–10-cc. portions of $CHCl_3$. Distil very slowly at low temperature to about a quarter of the original volume. Then transfer the residue to a porcelain evaporating dish, rinsing the flask three times with 5–10-cc. portions of $CHCl_3$, and evaporate to dryness at room temperature in a current of dry air.

Dry the residue overnight (or until no odor of acetic acid can be detected, if the product is a ketchup) in a desiccator over conc. H_2SO_4. Dissolve the residue of benzoic acid in 30–50 cc. of neutral 95% alcohol, add about $\frac{1}{4}$ its volume of water and 1 or 2 drops of phenolphthalein, and titrate with 0.05 N NaOH.

CALCULATION.—1 cc. 0.05 N NaOH
= 0.0072 gram anhydrous Na-benzoate.
= 0.0061 gram anhydrous benzoic acid.

REFERENCE.—Association of Official Agricultural Chemists: "Methods of Analysis," 127 (1925).

SALICYLIC ACID IN FOODS

Preparation of Sample.—NON-ALCOHOLIC LIQUIDS.—Many liquids may be extracted directly as directed below under the Ferric Chloride Test or the Colorimetric Test without further treatment. If troublesome emulsions form during extraction, pipette 100 cc. into a 250-cc. volumetric flask, add about 5 grams of NaCl, shake until the latter is dissolved, dilute to the mark with 95% alcohol, shake vigorously, let the mixture stand 10 minutes with occasional shaking, filter through a dry folded filter, and treat an aliquot of the filtrate as described in the next paragraph.

ALCOHOLIC LIQUIDS.—Make 200 cc. of the sample alkaline to litmus with 10% NaOH solution, and evaporate on the steam bath to about $\frac{1}{3}$ the original volume. Dilute to the original volume with water and filter, if necessary.

SOLID OR SEMISOLID SUBSTANCES.—Grind the sample and mix thoroughly. Transfer a convenient quantity (50–200 grams according to the consistency of the sample) to a 500-cc. volumetric flask, dilute to about 400 cc., shake until the mixture becomes uniform, add 2–5 grams of $CaCl_2$, shake until the latter is dissolved, render distinctly alkaline to litmus with 10% NaOH

solution, fill to the mark with water, shake thoroughly, let stand for at least 2 hours, shaking frequently, and filter.

Qualitative Tests.—Ferric Chloride Test.—Introduce 50 cc. of the sample or an equivalent amount of an aqueous extract, prepared as directed above, into a separatory funnel; add $\frac{1}{10}$ its volume of dil. HCl (1 : 3) and extract with 50–100 cc. of ether. If the mixture emulsifies, add 10–15 cc. of petroleum ether (b.p. below 60° C.) and shake. If this treatment fails to break the emulsion, whirl the mixture in a centrifuge, or let stand until a considerable portion of the aqueous layer has separated, run off the latter, shake vigorously and again let separate. Wash the ether layer with two 5-cc. portions of water, evaporate the greater portion of the ether in a porcelain dish on the steam bath, let the remainder evaporate spontaneously and add a drop of 0.5% $FeCl_3$ solution. A violet color indicates salicylic acid.

If coloring matter or other interfering substances are present in the residue left after evaporation of the ether, purify the salicylic acid by one of the following methods:

(*a*) Dissolve the original residue from the ether extract, obtained as directed above, in about 25 cc. of ether; transfer to a separatory funnel and shake with an equal volume of water, made distinctly alkaline with several drops of conc. NH_4OH. Let separate, filter the aqueous layer through a wet filter into a porcelain dish, evaporate almost to dryness, and test the residue as directed above.

(*b*) Dry the original residue from the ether extract in a desiccator over conc. H_2SO_4 and extract with several 10-cc. portions of CS_2 or petroleum ether (b.p. below 60° C.), rubbing the contents of the dish with a glass rod, and filtering the successive portions of the solvent through a dry paper into a second porcelain dish. Evaporate the greater portion of the solvent on the steam bath, let the remainder evaporate spontaneously, and test the residue as directed above.

(*c*) Transfer the original residue from the ether extract to a small porcelain crucible by means of a few cc. of ether and let the solvent evaporate spontaneously. Cut a hole in a piece of asbestos board sufficiently large to admit about $\frac{2}{3}$ of the crucible, cover the latter with a small, round-bottomed flask filled with cold water, and heat over a small flame until any salicylic acid present

has sublimed and condensed upon the bottom of the flask. Test the sublimate as directed above.

JORISSEN'S TEST.—Dissolve the residue from the ether extract, obtained as previously directed under Ferric Chloride Test, or, in case impurities are present, the purified material obtained as there directed, in a little hot water. Cool 10 cc. of the solution in a test-tube, add 4 or 5 drops of 10% KNO_2 solution, 4 or 5 drops of 50% acetic acid and 1 drop of 10% $CuSO_4$ solution, mix thoroughly and heat to boiling. Boil for $\frac{1}{2}$ minute and let stand for 1–2 minutes. In the presence of salicylic acid a blood-red color will develop.

Quantitative Determination (Colorimetric).—EXTRACTION.—Pipette 100 cc. of the sample or a volume of the solution, prepared as previously described, representing not less than 20 grams of the original, into a separatory funnel. Make neutral to litmus with dil. HCl (1:3) and add an excess of conc. HCl equivalent to 2 cc. of acid for each 100 cc. of solution. Extract with 4 separate portions of ether, using for each extraction an amount equivalent to half the volume of the aqueous layer. If an emulsion forms on shaking, this may usually be broken by adding a little ($\frac{1}{5}$ the volume of the ether layer) petroleum ether (b.p. below 60° C.) and shaking again, or by centrifugalizing. If a little of the emulsion still persists, let it remain with the aqueous layer. If an emulsion remains after the fourth extraction, separate it from the clear ether and the clear aqueous layer and extract it separately with 2–3 small portions of ether. Combine the ether extracts, wash with $\frac{1}{10}$ their volume of water, let the layers separate, and reject the aqueous layer. Wash in this way until the aqueous layer after separation yields a yellow color upon the addition of methyl orange and 2 drops of 0.1 N NaOH. Distil slowly the greater part of the ether, transfer the remainder to a porcelain dish and let the ether evaporate spontaneously. If there are no interfering substances present, proceed as below under Determination; otherwise purify the residue by one of the following methods:

(*a*) Dry the residue thoroughly *in vacuo* over conc. H_2SO_4 and extract with 10 portions of 10–15 cc. each of CS_2 or petroleum ether (b.p. below 60° C.); rub the contents of the dish with a glass rod and filter the successive portions of the solvent through

a dry filter into a porcelain dish. Test the extracted residue with a drop of 2% ferric alum solution and, if it gives a reaction for salicylic acid, dissolve it in water, acidify the solution with dil. HCl (1:3), extract with ether, evaporate, extract the dry residue thus obtained with CS_2 or petroleum ether and add to the extract first obtained. Distil the greater portion of the CS_2 or petroleum ether and let the remainder evaporate spontaneously. Proceed as directed below under Determination.

(*b*) Dissolve the residue in 40–50 cc. of ether. Transfer the ether solution to a separatory funnel and extract with 3 successive 15-cc. portions of 1% NH_4OH. (If fat is known to be present in the original ether extract, extract the latter directly with 4 portions of the NH_4OH instead of 3.) Combine the alkaline aqueous extracts, acidify, again extract with ether, and wash the combined ether extracts as directed above. Distil slowly the greater portion of the ether, let the remainder evaporate spontaneously and proceed as directed below.

Determination.—Dissolve the residue obtained above in a small amount of hot water and, after cooling, dilute to a definite volume (usually 50 or 100 cc.), dependent on the amount of salicylic acid present. If the solution is not clear, filter through a dry filter. Dilute aliquots of the solution and treat with a few drops of 0.5% $FeCl_3$ solution or 2% ferric alum solution* until the maximum color is developed. Generally a few drops will be sufficient. Compare the colors developed with the color obtained when a standard salicylic acid solution (containing 1 mg. of salicylic acid in 50 cc.) is similarly treated, using Nessler tubes or a colorimeter. In either case, and especially with $FeCl_3$, avoid an excess of the reagent, although an excess of 0.5 cc. of 2% ferric alum solution may be added to 50 cc. of the comparison solution of salicylic acid without impairing the results.

Reference.—This is the official method of the Association of Official Agricultural Chemists as published in its "Methods of Analysis," 125 (1925).

* The ferric alum solution should be boiled until a precipitate appears, allowed to settle, and filtered. The acidity of the solution is slightly increased in this manner, but it remains clear for a considerable time, and the turbidity caused by its dilution with water is much less and does not appear as soon as when the unboiled solution is used. This turbidity interferes with the exact matching of the color.

FORMIC ACID IN FOODS

Reagents.—(*a*) *Sodium Acetate Solution.*—Dissolve 50 grams of dry sodium acetate in sufficient water to make 100 cc., and filter.

(*b*) *Mercuric Chloride Reagent.*—Dissolve 100 grams of $HgCl_2$ and 150 grams of NaCl in sufficient water to make 1 liter, and filter.

(*c*) *Dilute HCl.*—Approximately 10% solution; dilute 30 cc. of conc. HCl with 70 cc. of water.

Apparatus.—The apparatus required (Fig. 32) consists of a steam generator *S*; a 300-cc. flask *A*, in which the sample is

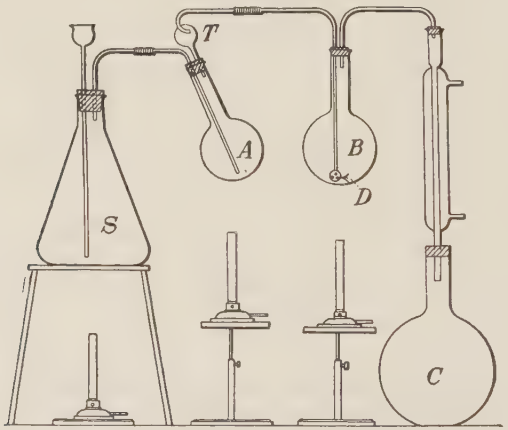


Fig. 32.—Apparatus for Determination of Formic Acid.

placed; a 500-cc. flask *B*, containing a suspension of $BaCO_3$; a spray trap *T*; a condenser; and a 1-liter volumetric flask *C*. The tip of the tube *D*, leading into *B*, consists of a bulb containing a number of small holes to break the vapor into small bubbles.

Determination.—For thin liquids, like fruit juices, use 50 cc.; for heavy liquids and semisolids, like syrups and jams, use 50 grams diluted with 50 cc. of water. Place the sample in the flask *A*, add 1 gram of tartaric acid, and connect as indicated, the flask *B* having been charged previously with a suspension of 2 grams of $BaCO_3$ in 100 cc. of water. If much acetic acid is present, sufficient $BaCO_3$ must be used so that at least 1 gram

remains at the end of the operation. Heat the contents of flasks *A* and *B* to boiling and distill with steam from the generator *S*, the vapor passing first through the sample in flask *A*, then through the boiling suspension of $BaCO_3$ in *B*, after which it is condensed, and measured in the volumetric flask *C*. Continue the distillation until 1 liter of distillate is collected, maintaining the volume of the liquids in flasks *A* and *B* as nearly constant as possible by heating with small Bunsen flames, and avoiding charring of the sample in the flask *A*.

After 1 liter of distillate has been collected, disconnect the apparatus and filter the contents of flask *B* while hot, washing the $BaCO_3$ with a little hot water. The filtrate and washings should now measure about 150 cc. If not, boil down to that volume. Then add 10 cc. of the sodium acetate solution, 2 cc. of the dil. HCl, and 25 cc. of the $HgCl_2$ reagent. Mix thoroughly and immerse the container in a boiling water or steam bath for 2 hours. Then filter on a tared Gooch crucible and wash the precipitate thoroughly with cold water and finally with a little alcohol. Dry in a boiling water oven for 30 minutes, cool, weigh, and calculate the weight of formic acid present by multiplying the weight of the Hg_2Cl_2 precipitate by 0.0975.

NOTE. –If the weight of Hg_2Cl_2 obtained exceeds 1.5 grams, repeat the determination, using more $HgCl_2$ reagent or a smaller amount of sample. Conduct a blank test with each new lot of reagents employed in the reduction, using 150 cc. of water, 1 cc. of 10% $BaCl_2$ solution, 2 cc. of the dil. HCl, 10 cc. of the Na acetate, and 25 cc. of the $HgCl_2$ reagent, and heat the mixture in a boiling water or steam bath for 2 hours. Deduct the weight of Hg_2Cl_2 obtained in this blank test from that obtained in the regular determination.

REFERENCE.—Association of Official Agricultural Chemists: "Methods of Analysis," 137 (1925).

BORIC ACID AND BORATES IN FOODS

Qualitative Test.—(*a*) *Preliminary.*—Immerse a strip of turmeric paper in the sample acidified with HCl in the proportion of 7 cc. of conc. HCl to each 100 cc. of sample, and let the paper dry spontaneously. If borax or boric acid is present, the paper will acquire a characteristic red color, changed by NH_4OH or Na_2CO_3 solution to a dark blue-green but restored by acid. In case of solid or pasty samples heat with enough water to make them sufficiently fluid before acidifying.

(*b*) *Confirmatory.*—Make about 25 grams of the sample decidedly alkaline with lime water and evaporate to dryness on the steam bath. Ignite the residue at a low red heat until the organic matter is well charred. Digest with about 15 cc. of water, and add conc. HCl, drop by drop, until the solution is distinctly acid. Saturate a piece of turmeric paper with the solution, and let it dry without heat. In the presence of borax or boric acid, the color change will be the same as given above.

Quantitative Determination.—Make 10–100 grams of the sample (depending upon its nature and the amount of H_3BO_3 present) distinctly alkaline with NaOH solution and evaporate to dryness in a platinum dish. Ignite the residue until the organic matter is well charred, avoiding an intense red heat; cool, digest with about 20 cc. of hot water, and add conc. HCl, drop by drop, until distinctly acid. Filter into a 100-cc. volumetric flask, and wash with a little hot water, the volume of the filtrate not to exceed 50–60 cc. Return the filter containing any unburned carbon to the platinum dish, make alkaline by wetting thoroughly with lime water, dry on the steam bath, and ignite to a white ash. Dissolve the ash in a few cc. of dil. HCl (1:3) and add to the liquid in the 100-cc. flask, rinsing the dish with a few cc. of water. To the combined solutions, add 0.5 grams of $CaCl_2$ and a few drops of phenolphthalein indicator, then 10% NaOH solution until a permanent light pink color is produced, and finally dilute to the mark with lime water. Mix and filter through a dry filter.

To 50 cc. of the filtrate add 1.0 N H_2SO_4 until the pink color disappears, then add methyl orange, and continue the addition of acid until the yellow color is changed to pink. Boil for about 1 minute to expel CO_2. Cool, and carefully add 0.2 N NaOH until the liquid assumes a yellow tinge, avoiding an excess of the alkali. All the H_3BO_3 is now in a free state with no uncombined H_2SO_4 present. Add about 10 grams of neutral mannitol (mannite) and a few drops of phenolphthalein indicator and titrate with 0.2 N NaOH until a permanent pink color is produced. At the end of the titration add about 2 grams more of mannitol and continue the titration if the pink color is discharged. Repeat the alternate addition of mannitol and 0.2 N NaOH until a permanent pink end-point is reached. (A volume of neutral

glycerol equal to the volume of the solution to be titrated may be substituted for the mannitol but the end-point is not so sharp.) Calculate the total titration after the first addition of mannitol to boric acid or borax as desired.

CALCULATION.—1 cc. 0.2 N NaOH = 0.01237 gram H_3BO_3.
= 0.01006 gram $Na_2B_4O_7$.
= 0.01907 gram $Na_2B_4O_7 \cdot 10H_2O$.

REFERENCE.—Association of Official Agricultural Chemists: "Methods of Analysis," 131 (1925).

ARTIFICIAL SWEETENERS IN FOODS

Saccharin.—PREPARATION OF SAMPLE.—(*a*) *Fruit Juices, Syrups, and Other Non-alcoholic Liquids.*—Transfer 100–200 grams of the sample to a 250-cc. volumetric flask by means of a little water, dilute to about 200 cc. with water, add 5 cc. of glacial acetic acid, mix, add a slight excess of 20% *neutral* lead acetate solution, mix thoroughly, dilute to the mark with water, again mix thoroughly and filter through a folded filter.

(*b*) *Alcoholic Liquids.*—Heat 100–200 cc. of the liquid on a steam bath to remove alochol, this being accomplished in most cases by evaporating to $\frac{1}{2}$ the original volume. In the case of heavy syrups dilute the liquid with an equal volume of water before beginning the evaporation. After the alcohol has been removed, transfer to a 250-cc. volumetric flask and proceed from this point as directed above under (*a*).

(*c*) *Solid or Semisolid Preparations.*—Transfer 50–75 grams of the sample to a 250-cc. volumetric flask by means of a little hot water and add sufficient nearly boiling water to make the volume about 200 cc. Let the mixture stand for 2 hours, shaking occasionally. Then add 5 cc. of glacial acetic acid, mix thoroughly, add a slight excess of 20% *neutral* lead acetate solution, dilute to the mark with cold water, mix and let stand for 20 minutes. Filter through a folded filter.

QUALITATIVE TEST.—Acidify 50 cc. of a non-alcoholic liquid food or an equivalent quantity of an aqueous extract, prepared as directed previously, with conc. HCl and extract 3 times with 25-cc. portions of ether. Wash the combined ether extract once

with 5 cc. of water, transfer to a small beaker or evaporating dish and let the ether evaporate spontaneously. Dissolve the residue in a little hot water and test a small portion of the solution for salicylic acid (see p. 535). Dilute the remainder of the solution to about 10 cc. and add 2 cc. of dil. H_2SO_4 (1:3). Heat to boiling and add a slight excess of 5% $KMnO_4$ solution, drop by drop. Partly cool the solution, dissolve about 1 gram of NaOH in it, and filter the mixture into a silver dish (silver crucible lids are suitable). Evaporate to dryness and heat for 20 minutes at 210–215° C. Dissolve the residue in water, acidify with HCl and test the ether extract for salicylic acid as previously described. By this method all the so-called "false saccharin" and the salicylic acid naturally present (also added salicylic acid when not present in too large an amount) are destroyed, while 5 milligrams of saccharin per liter are detected with certainty.

Quantitative Determination.—Transfer 150 cc. of the filtrate (obtained by one of the methods for Preparation of Sample) to a separatory funnel, add 15 cc. of conc. HCl, and extract three times with 80-cc. portions of ether, shaking the separatory funnel for 2 minutes each time. Wash the combined ether extracts once with 5 cc. of water, remove the ether by distillation and transfer the residue to a platinum crucible by means of a little ether; or, if substances difficultly soluble in ether are present, use alternately small portions of water and ether. Evaporate the ether on the steam bath, add to the residue 2–3 cc. (or enough to make the mixtures strongly alkaline) of a 10% Na_2CO_3 solution, rotate so that all the saccharin is brought in contact with the solution and evaporate to dryness on the steam bath. To the dry residue in the crucible add 4 grams of a mixture of equal parts of anhydrous Na_2CO_3 and K_2CO_3, heat gently at first and then to complete fusion for 30 minutes over an alcohol or other sulfur-free flame. The fusion may be conducted with a gas flame by closely fitting the crucible into a hole cut into a piece of heavy asbestos board so that $\frac{1}{3}$ of the crucible projects above the asbestos, and heating the lower portion of the crucible by means of a large Bunsen or Meker burner.

Cool, dissolve the melt in water, add about 5 cc. of Br water, acidify with conc. HCl, filter, wash the paper with a little water, dilute the filtrate and washings to about 200 cc., heat to boiling,

and slowly add an excess of 10% $BaCl_2$ solution. Let stand overnight, collect the $BaSO_4$ on a filter (or a platinum Gooch crucible), wash until free from Cl, dry, ignite, cool and weigh. Correct the result thus obtained for any sulfur present in the fusion mixture as found by a blank determination. Calculate the equivalent amount of saccharin ($C_7H_5SO_3N$) from the corrected weight of $BaSO_4$.

CALCULATION.—$BaSO_4 \times 0.7844 = Saccharin$.

NOTES.—(1) Instead of the mixed Na_2CO_3 and K_2CO_3, 3–4 grams of Na_2O_2 may be employed for the fusion. In this case a nickel crucible must be used, and the time of fusion may be reduced to 5 minutes.

(2) The separation of a little $PbCl_2$ during the extraction does not interfere with the accuracy of the method.

Dulcin.—*Morpurgo Qualitative Test.*—Evaporate about 100 cc. of the sample, or of the aqueous extract prepared as directed under Salicylic Acid (p. 534, Solid or Semisolid Substances) and neutralized with acetic acid, to a sirupy consistency after the addition of about 5 grams of $PbCO_3$, and extract the residue several times with 90% alcohol. Evaporate the alcoholic extract to dryness, extract the residue with ether, and let the ether evaporate spontaneously in a porcelain dish. Add 2 or 3 drops each of phenol and conc. H_2SO_4 and heat for about 5 minutes on the water bath; cool, transfer to a test-tube and overlay with conc. NH_4OH or NaOH solution with the least possible mixing. The presence of dulcin is indicated by the formation of a blue color at the zone of contact.

Sucrol.—*Jorissen Qualitative Test.*—Suspend the residue from the ether extract, obtained as directed above, in about 5 cc. of water; add 2–4 cc. of an approximately 10% solution of $Hg(NO_3)_2$, and heat for 5–10 minutes on the steam bath. In the presence of sucrol a violet-blue color is formed, which is changed to deep violet on the addition of PbO_2.

REFERENCE.—Association of Official Agricultural Chemists: "Methods of Analysis," 129 and 136 (1925).

REDUCING SUGARS AND SUCROSE

General.—This method describes general procedures to be used in determining sucrose and different kinds of reducing sugars in various materials. In employing these methods, however, the

analyst should make sure that there are not special methods or precautions to be used with the particular substances under analysis.

The methods described below are official methods of the Association of Official Agricultural Chemists, unless otherwise designated.

(I) Sucrose

There are 2 general classes of methods for the determination of sucrose: (1) Optical methods, and (2) Chemical methods.

(1) **Optical Methods.**—The rules of the International Commission for Unifying Methods of Sugar Analysis have been adopted as an official method of the Association of Official Agricultural Chemists for *raw sugars* as follows:

General Directions for Raw Sugars.—"In general, all polarizations are to be made at 20° C. The verification of the saccharimeter must also be made at 20° C. For instruments using the Ventzke scale 26 grams of pure dry sucrose, weighed in air with brass weights, dissolved in water so that 100 metric cc. of solution is obtained at 20° C., and polarized in a room or cabinet, the temperature of which is also 20° C., must give a saccharimeter reading of exactly 100.00. The temperature of the sugar solution during polarization must be kept constant at 20° C.*

"For countries where the mean temperature is higher than 20° C., saccharimeters may be adjusted at 30° C. or any other suitable temperature, under the conditions specified above, provided the sugar solution be diluted to final volume and polarized at this same temperature.

"In determining the polarization of substances containing sugar employ only half-shade instruments." The saccharimeter used may be either single or double wedge and should be a half-shadow instrument with either double or triple field.

"During the observation keep the apparatus in a fixed position and so far removed from the source of light that the polarizing Nicol is not warmed. As sources of light employ lamps which

* According to Bates and Jackson of the U. S. Bur. of Standards, *J. Ind. Eng. Chem.*, **12,** 792 (1920), the Ventzke reading for 26 grams of pure dry sucrose under these conditions is 99.89 instead of 100.00

give a strong illumination, such as triple gas burner with metallic cylinder, lens and reflector; gas lamps with Auer (Welsbach) burner; electric lamp; petroleum duplex lamp; or sodium light. Whenever there is any irregularity in the sources of light, such as that due to the convolutions of the filament in the case of an electric light or to the meshes of the gauze in the case of the Welsbach light, place a thin ground-glass plate between the source of light and the polariscope, so as to render the illumination uniform.

"Before and after each set of observations the chemist must satisfy himself of the correct adjustment of his saccharimeter by means of standardized quartz plates. He must also previously satisfy himself of the accuracy of his weights, polarization flasks, observation tubes and cover-glasses. (Scratched cover-glasses must not be used.) Make several readings and take the mean thereof, but no one reading may be neglected." The quartz plates are standardized to read to the second decimal place and by their use a quick and at the same time accurate test can be made. In using such plates for testing saccharimeters, it is necessary that the instrument, as well as the plate, be at 20° C. before making a reading. Different points of the scale, preferably 20°, 50°, 80°, and 100° (sugar scale) should be tested against the plates.

"In determining the polarization use the whole normal weight for 100 cc. or a multiple thereof for any corresponding volume.

"As clarifying and decolorizing agents use either basic acetate of lead, alumina cream, or concentrated solution of alum. Bone-black and decolorizing powders are to be excluded." *Whenever reducing sugars are determined in the solution for polarizing, use only neutral lead acetate for clarification, as basic lead acetate causes precipitation of some of the reducing sugars.* In addition to these clarifying agents, basic lead nitrate (Herles' solution) has been made official by the Association.

"After bringing the solution exactly to the mark at the proper temperature, and after wiping out the neck of the flask with filter paper, pour all of the well-shaken clarified sugar solution on a rapidly acting, dry filter. Reject the first portions of the filtrate, and use the rest, which must be perfectly clear, for polarization." It is advisable to reject the first 25 cc. that run through, then cover the funnel with a watch glass and use the remainder for

polarization. In no case should the whole solution or any part be returned to the filter. If cloudy after the 25 cc. have been rejected, begin a new determination.

"Whenever white light is used in polarimetric determinations, the same must be filtered through a solution of $K_2Cr_2O_7$ of such a concentration that the percentage content of the solution multiplied by the length of the column of the solution in centimeters is equal to 9." This concentration must be doubled in polarizing carbohydrate materials of high rotation dispersion, such as commercial glucose, etc.

Preparation and Use of Clarifying Reagents.—(*a*) *Basic lead acetate solution.*—Boil 430 grams of neutral lead acetate, 130 grams of litharge, and 1 liter of water for 30 minutes. Let the mixture cool and settle, and dilute the supernatant liquid to sp. gr. 1.25 with recently boiled water. Solid basic lead acetate may be substituted for the normal salt and litharge in the preparation of the solution.

(*b*) *Alumina cream.*—Prepare a cold saturated solution of alum (potassium aluminum sulfate) in water. Add conc. NH_4OH with constant stirring until the solution is alkaline to litmus; let the precipitate settle and wash by decantation with water until the wash water gives only a slight test for sulfates with $BaCl_2$ solution. Pour off the excess of water and store the residual cream in a stoppered bottle.

(*c*) *Dry basic lead acetate* (*Horne Method*).—This clarifying agent is obtained as a dry powdered salt and should contain 72.8% of Pb, which corresponds to a composition of $3Pb(C_2H_3O_2)_2 \cdot 2PbO$. In making the clarification, after diluting the sugar solution to volume in the flask, add a small quantity of the dry salt and shake, then add more and shake again, repeating until completely precipitated, but avoiding any excess. Of this salt 0.1346 gram is equivalent to 1 cc. of the basic lead acetate solution, described under (*a*). When molasses or any other substance producing a heavy precipitate is being clarified, add some dry, coarse sand to break up the balls of basic lead acetate and precipitate. (Dry basic lead acetate can also be used in place of a solution of basic lead acetate in clarifying cane, sorghum, and beet products.)

(*d*) *Neutral lead acetate.*—Prepare a saturated solution of neutral lead acetate and add it to the sugar solution before completing to volume. Its use is imperative when determining the reducing sugars in the solution used for polarization.

(*e*) *Basic lead nitrate (Herles' Solution).*—(1) Dissolve 250 grams of $Pb(NO_3)_2$ in water and make up to 500 cc. (2) Dissolve 25 grams of NaOH in water and make up to 500 cc. In making the clarification, add equal amounts of (1) and (2) to the sugar solution, shake, and add more if complete precipitation has not occurred, but avoid an excess. Then complete the volume with water. When this solution is used for clarification, the factor in the Clerget determination becomes 143.5.

Temperature Corrections for the Polarization of Sugars (Tentative).—(*a*) *Refined Sugars.*—The polarizations of sugars testing 99 or above, when made at temperatures other than 20° C., may be calculated to polarizations at 20° C. by the following formula:

$$P_{20°} = p^t[1+0.0003(t-20)],$$

in which p^t = the polarization at the temperature read;
and t = the temperature at which the polarization is read.

(*b*) *Raw Cane Sugars.*—The polarizations of raw cane sugars, when made at temperatures other than 20° C., may be calculated to polarizations at 20° C. by the following formula:

$$P_{20°} = p^t+0.0015(p^t-80)(t-20),$$

in which p^t and t are the same as in the formula under (*a*).

When the percentage of levulose in the sugar is known (which in the case of honeys and sugar cane products is approximately one-half the reducing sugars), the following formula should be used:

$$P_{20°} = p^t+0.0003S(t-20)-0.00812L(t-20),$$

in which p^t and t are the same as in the formula under (*a*);

S = the percentage of sucrose; and
L = the percentage of levulose.

These formulas give results agreeing closely with the polarizations obtained at 20° C. if the sugar is of average normal composition.

MUTAROTATION.—Products, such as honey and commercial glucose, that contain dextrose or other reducing sugars in crystalline form or in solution at high density, may exhibit the phenomenon of mutarotation under the conditions prevailing during analysis. Only the constant rotation should be employed in polarimetric methods. To obtain this, allow the solution prepared for polarization to stand overnight before making the reading. If it is desired to make the reading immediately, heat the neutral (pH approximately 7.0)* solution to boiling for a few moments or add a few drops of conc. NH_4OH before completing to volume; or, if the solution has been made to volume, add dry Na_2CO_3 until just distinctly alkaline to litmus paper. (Do not allow the slightly alkaline solutions to stand at such high temperatures or for such lengths of time as to cause destruction of fructose.) Determine the completion of mutarotation by making readings at 15–30-minute intervals until these become constant.

DETERMINATION OF SUCROSE IN THE ABSENCE OF RAFFINOSE BY POLARIZATION BEFORE AND AFTER INVERSION WITH HCL (TENTATIVE).†—(*a*) *Direct Reading.*—Dissolve the double normal weight (52 grams) of the substance in water in a 200-cc. volumetric flask, add basic lead acetate carefully, avoiding any excess, then 1–2 cc. of alumina cream, shake and dilute to 200 cc. Mix well, filter, rejecting the first 25 cc. of the filtrate, cover the funnel with a watch glass and, when sufficient filtrate is collected, remove the Pb from the solution by adding anhydrous Na_2CO_3, a little at a time, avoiding any excess; mix well and filter again, rejecting at least the first 25 cc. of the filtrate.‡ Pipette one 50-cc. portion of the Pb-free filtrate into a 100-cc. volumetric flask, dilute to the mark with water, mix well and polarize in a 200-mm. tube. The reading, multiplied by 2, is the direct

* See page 739.

† In the presence of much levulose, as in honeys, fruit products, sorghum syrup, cane syrup and molasses, the optical method for sucrose, requiring hydrolysis by acid, gives erroneous results.

‡ Instead of weighing 52 grams into a 200-cc. flask, two 26-gram portions may be diluted to 100 cc. each and treated exactly as described. Depending upon the color of the product, multiples or fractions of the normal weight may be used, and the results reduced by calculation to the basis of 26 grams in 100 cc.

reading (P of the formula given below) or polarization before inversion. If there is a possibility of mutarotation, see page 548.

(*b*) *Invert Reading.*—For the invert reading, introduce 50 cc. of the lead-free filtrate into a 100-cc. volumetric flask and add 25 cc. of water. Then add, little by little, while rotating the flask, 6 cc. of conc. HCl. Place a thermometer in the flask, and heat, with constant agitation, in a water bath kept at 70° C. The temperature of the solution in the flask should reach 67° C. in 2.5–3.75 minutes. From the moment the thermometer in the flask reaches 67° C., leave the flask in the bath for exactly 5 minutes, during which time the temperature should gradually rise to about 69.5° C. Plunge the flask at once into water at 20° C. When the contents have cooled to about 35° C., remove the thermometer, rinse it into the flask and fill almost to the mark with water. Leave the flask in the bath at 20° C. for at least 30 minutes more and finally dilute exactly to volume. Polarize this solution in a tube provided with a lateral branch and water jacket, keeping at 20° C. This reading must be doubled to obtain the invert reading. If necessary to work at a temperature other than 20° C., which is allowable within narrow limits, the volumes must be completed and both direct and invert polarizations must be made at exactly the same temperature.

Calculate the sucrose by the following formula (Clerget):

$$S = \frac{100(P-I)}{143+0.0676(m-13)-\frac{T}{2}},$$

in which S = percentage of sucrose;

P = direct reading of normal solution;

I = invert reading of normal solution;

T = temperature at which readings are made;

and m = grams of total solids in 100 cc. of the invert solution read in the polariscope.*

(*c*) *Inversion at Room Temperature.*—The inversion may also be accomplished as follows: (1) To 50 cc. of the clarified solution, freed from Pb, add 6 cc. of conc. HCl and set aside for 24 hours at a temperature not below 20° C.; or, (2) if the temperature be

* Obtained by determining the total solids as percentage by weight, as described on page 560, and multiplying this figure by the sp. gr. at 20° C.

above 25° C., set aside for 10 hours. Make up to 100 cc. at 20° C. and polarize as directed above.

Under these conditions the previous Clerget formula must be changed to the following:

$$S = \frac{100(P-I)}{143.2+0.0676(m-13)-\frac{T}{2}}.$$

Determination of Sucrose and Raffinose (of value chiefly in analysis of beet products).—If the direct reading is more than 1° higher than the percentage of sucrose as calculated by the formula given above, raffinose is probably present. Calculate sucrose and raffinose by the following formulas of Herzfeld:

$$S = \frac{0.514P-I}{0.844} \text{ and } R = \frac{0.33P+I}{1.563},$$

in which P = direct reading of normal solution;
I = invert reading of normal solution;
S = percentage of sucrose;
and R = percentage of anhydrous raffinose.

The above formulas assume that polarizations are made at exactly 20° C. If the temperature (T) is other than 20° C., the following formulas should be used:

$$S = \frac{P(0.478+0.0018t)-I(1.006-0.0003T)}{(0.908-0.0032t)(1.006-0.0003T)}$$

and

$$R = \frac{P(0.43-0.005t)+I(1.006-0.0003T)}{(1.681-0.0059t)(1.006-0.0003T)};$$

in which P = direct reading of normal solution,
I = invert reading of normal solution,
S = percentage of sucrose,
R = percentage of anhydrous raffinose,
T = temperature of direct polarization,
and t = temperature of invert polarization.

(2) **Chemical Method.**—Determination of Sucrose from Reducing Sugars before and after Inversion.—Determine the reducing sugars (clarification having been effected with *neutral* lead acetate, never with basic lead acetate), as directed below under the Munson and Walker Method and calculate to invert sugar from the M. and W. tables. Then invert the solution

as directed above (under Polarization before and after Inversion with HCl), exactly neutralize the acid and again determine the reducing sugars; but calculate them to invert sugar from the same table as just referred to, using the invert sugar column alone. Deduct the percentage of invert sugar determined before inversion from that obtained after inversion, and multiply the difference by 0.95; the result is the percentage of Sucrose. The solution should be diluted in both determinations so that not more than 240 milligrams of invert sugar are present in the amount taken for reduction. It is also important that all Pb be removed from the solution with anhydrous powdered $K_2C_2O_4$ or Na_2CO_3 before reduction.

(II) Total Reducing Sugars

General.—The determination of reducing sugars by copper reduction depends upon the reduction of an alkaline copper solution by the action of the reducing sugars, precipitating red Cu_2O. Since the extent of the reduction varies under different conditions, it is necessary that the directions be *strictly adhered to.*

Of the common sugars, sucrose is the only one which has no direct reducing action on alkaline copper tartrate; but on undergoing inversion, it is converted into reducing sugars which can be readily determined.

There are various methods, all based on the reduction of Cu salts, but varying in detail. For all ordinary use the Munson and Walker method is the most convenient, since the Cu_2O can be calculated directly to dextrose, invert sugar, maltose or lactose, as the case may be. It is not well adapted, however, to the determination of lactose (milk sugar) in the presence of sucrose, for instance in sweetened condensed milk or in sweetened milk chocolate, on account of partial inversion of the sucrose by the boiling. In such case it is preferable to use the Defren-O'Sullivan method.

Munson and Walker Method.—Reagents.—(*a*) *Fehling's Copper Sulfate Solution.**—Dissolve 34.639 grams of carefully selected crystals of pure $CuSO_4 \cdot 5H_2O$ in water, dilute to exactly 500 cc. and filter through prepared asbestos.

* Soxhlet modification.

(*b*) *Fehling's Alkaline Tartrate Solution.**—Dissolve 173 grams of Rochelle salts ($KNaC_4H_4O_6 \cdot 4H_2O$) and 50 grams of NaOH in water, dilute to exactly 500 cc., let stand for 2 days, and filter through prepared asbestos.

(*c*) *Asbestos.*—Digest the asbestos (which should be of the amphibole variety) with dil. HCl (1:3) for 2–3 days. Wash free from acid and digest for a similar period with 10% NaOH solution. Then treat for a few hours with hot alkaline tartrate solution of the strength employed in the sugar determinations. (Old alkaline tartrate solutions that have stood for some time may be used.) Then wash free from alkali, digest with dil. HNO_3 (1:3) for several hours, and, after washing free from acid, shake with water into a fine pulp. In preparing the Gooch crucible, make a film of asbestos 0.25 inch thick and wash thoroughly with water to remove fine particles of asbestos. Finally wash with alcohol and then with ether. Dry for 30 minutes at 100° C., cool in a desiccator and weigh. It is best to dissolve the Cu_2O with HNO_3 each time after weighing and use the same felts repeatedly, as they improve with use.

Procedure.—Transfer 25 cc. each of the copper sulfate and the alkaline tartrate solutions to a 400-cc. beaker of alkali-resisting glass, and add 50 cc. of the reducing sugar solution, which must be neutral or slightly alkaline; or, if a smaller volume of sugar solution be used, add water to make the final volume 100 cc. Heat the beaker on an asbestos gauze over a Bunsen burner; so regulate the flame that boiling begins in 4 minutes, and continue boiling for exactly 2 minutes.†

Keep the beaker covered with a watch glass throughout the heating. Without diluting, filter the Cu_2O at once on the asbestos felt in a porcelain Gooch crucible, using suction. Wash the Cu_2O thoroughly with water at about 60° C., then with 10 cc. of alcohol, and finally with 10 cc. of ether. Dry for 30 minutes in the water oven at 100° C., cool in a desiccator and weigh as Cu_2O.

Calculate from the weight of the Cu_2O (see note 3 below) the amount of reducing sugars according to Munson and Walker's

* Soxhlet modification.

† It is important that these directions be strictly observed. In order to regulate the burner for this purpose, it is advisable to make preliminary tests, using 50 cc. of the reagent and 50 cc. of water, before proceeding with the actual determination.

tables. These tables may be found in Leach: "Food Inspection and Analysis," 4th ed., page 623; also in Association of Official Agricultural Chemists: "Methods of Analysis," pages 434–445 (1925).

NOTES.—(1) The number of milligrams of Cu reduced by a given amount of reducing sugar differs when sucrose is present and when it is absent. In the tables, the absence of sucrose is assumed, except in the columns under invert sugar and sucrose, and lactose and sucrose.

(2) *Blank Determination:* Always conduct a blank determination, using 50 cc. of the reagent and 50 cc. of water; and if the weight of the Cu_2O obtained exceeds 0.0005 gram, correct the result of the reducing sugar determination accordingly. The alkaline tartrate solution deteriorates on standing and the amount of Cu_2O obtained in the blank increases.

(3) The method of direct weighing of the Cu_2O should be used only for determinations in reducing sugar solutions of comparatively high purity; in all other cases the Cu of the Cu_2O should be determined by one of the following methods, since the Cu_2O is very apt to be contaminated with foreign matter.

DETERMINATION OF COPPER REDUCED.—

(*a*) *Electrolysis from H_2SO_4 Solution.*—Decant the hot solution through an asbestos mat in a Gooch crucible and wash the beaker and precipitate thoroughly with hot water without transferring the precipitate to the filter. Wash the asbestos film and adhering Cu_2O into the beaker by means of hot dil. HNO_3 (1:9). After all the Cu is in solution, refilter through a thin mat of asbestos in a Gooch crucible and wash thoroughly with hot water. Add 10 cc. of dil. H_2SO_4 (1:4) and evaporate the filtrate on the steam bath until the Cu salt has largely crystallized. Heat carefully on a hot plate or over asbestos until the evolution of white fumes shows that the excess of HNO_3 is removed. Add 8–10 drops of conc. HNO_3 and rinse into a 100–125-cc. platinum dish. Deposit the Cu upon the dish by electrolysis. Wash thoroughly with water, then break the current, wash with alcohol and ether successively, dry at about 50° C., and weigh. If preferred, the electrolysis may be conducted in a beaker, the Cu being deposited upon a weighed platinum electrode.

(*b*) *Electrolysis from H_2SO_4 and HNO_3 Solution.*—Filter and wash as directed above. Transfer the asbestos mat from the crucible to the beaker by means of a glass rod and rinse the crucible with about 30 cc. of a boiling mixture of dil. sulfuric

and nitric acids, containing 65 cc. of conc. H_2SO_4 and 50 cc. of conc. HNO_3 per liter. Heat and agitate until solution is complete; filter and electrolyze as above.

(*c*) *Electrolysis from HNO_3 Solution.*—Filter and wash as directed above. Transfer the asbestos mat and adhering Cu_2O to the beaker. Dissolve the oxide still remaining in the crucible by means of 2 cc. of conc. HNO_3, adding it with a pipette and collecting the solution in the beaker containing the asbestos. Rinse the crucible with a jet of water, letting the rinsings flow into the beaker. Heat the contents of the beaker until all Cu is in solution; filter, wash, dilute the filtrate to 100 cc. or more, and electrolyze. When a nitrate solution is electrolyzed, make the first washing of the deposit with water acidulated with H_2SO_4 in order to remove all HNO_3 before the current is interrupted.

Defren-O'Sullivan Method.*—Reagents.—The solutions used in this procedure are the same as those for the Munson and Walker method above described. The asbestos used should be of the long-fiber variety and should be specially prepared as follows: Boil first with dil. HNO_3 (about 1:6). Wash out the acid with hot water and then boil with a 25% solution of NaOH, and finally wash out the alkali with hot water. Keep the asbestos in a wide-mouthed flask or bottle and transfer it to the Gooch crucible by shaking up in the water and pouring it quickly into the crucible while under suction.

Procedure.—Mix 15 cc. of Fehling's $CuSO_4$ solution with 15 cc. of the tartrate solution in a 250-cc. Erlenmeyer flask, and add 50 cc. of distilled water. Place the flask and contents in a boiling water bath and let remain for 5 minutes. Then run rapidly from a burette into the hot liquor in the flask 25 cc. of the sugar solution to be tested (which should contain not over 0.5% of reducing sugars). Let the flask remain in the boiling water bath exactly 15 minutes after the addition of the sugar solution; remove, and with the aid of suction filter the contents rapidly in a Gooch crucible containing a layer of prepared asbestos fiber about 1 cm. thick, the Gooch crucible with the asbestos having been previously ignited, cooled and weighed. Wash the

* This method is described in Leach: "Food Inspection and Analysis," 4th ed., 618.

Cu_2O precipitate thoroughly with boiling water till the filtrate is no longer alkaline.

Dry the Gooch crucible with contents in the oven, and finally heat to dull redness for 15 minutes, during which the red Cu_2O is converted into black CuO. If a platinum Gooch crucible is used (which is preferable) it may be heated directly over the low flame of a burner. If the Gooch crucible is of porcelain, considerable care must be taken to avoid cracking, the heat being increased cautiously and the operation preferably conducted in a radiator or muffle. After oxidation as above, transfer the crucible to a desiccator, cool, and weigh quickly. From the milligrams of CuO, calculate the milligrams of dextrose, etc., as the case may be, and calculate to percentage of the original sample (see table in Leach, p. 619).

(III) Individual Reducing Sugars

Invert Sugar.—The methods for total reducing sugars previously given, also apply to the determination of invert sugar.* The following (Soxhlet) method is the tentative approximate volumetric method for rapid work of the Association of Official Agricultural Chemists.

Reagent: *Soxhlet's Modification of Fehling's Solution.*—Prepare by mixing, immediately before use, equal volumes of reagents (*a*) and (*b*) described previously under the Munson and Walker Method.

Standardization of Copper Solution.—Since the factor for calculation varies with the minute details of manipulation, every operator must determine a factor for himself, using a known solution of the pure sugar that he desires to determine, and keeping the conditions the same as those used for the determination.

Standardize the solution for invert sugar as follows: Dissolve 4.75 grams of pure sucrose in 75 cc. of water, add 6 cc. of conc. HCl and invert as described previously under Polarization (Sucrose in the Absence of Raffinose, p. 548). Neutralize the acid with NaOH solution and dilute to 1 liter. Ten cc. of this solution contain 0.050 gram of invert sugar, which should reduce 10 cc. of the reagent. The strength of the copper solution should

* See also under Levulose, Invert Sugar, etc. on p. 557.

never be taken as constant, but should be checked against the sugar.

DETERMINATION.—Place 10 cc. of the reagent in a large test-tube and add 10 cc. of water. Heat to boiling, and add gradually small portions of the solution of the material to be tested until the copper has been completely reduced, boiling after each addition to complete the reaction. Two minutes' boiling is required for complete reduction when the full amount of sugar solution has been added in one portion. When the end is nearly reached and the amount of sugar solution to be added can no longer be judged by the color of the solution, remove a small portion of the liquid and filter rapidly into a small porcelain crucible or on a test plate; acidify with dilute acetic acid, and test for Cu with dilute potassium ferrocyanide solution. The sugar solution should be of such strength as will give a burette reading of 15–20 cc. and the number of successive additions should be as small as possible.

Dextrose: Allihn's Gravimetric Method.—

REAGENT: *Allihn's Modification of Fehling's Solution.*

Prepare by mixing, immediately before use, equal volumes of (*a*) and (*b*), below.

(*a*) *Copper Sulfate Solution:* Dissolve 34.639 grams of $CuSO_4 \cdot 5H_2O$ in water and dilute to 500 cc.

(*b*) *Alkaline Tartrate Solution:* Dissolve 173 grams of Rochelle salts and 125 grams of KOH in water and dilute to 500 cc.

DETERMINATION.—Place 30 cc. of the $CuSO_4$ solution, 30 cc. of the alkaline tartrate solution and 60 cc. of water in a beaker and heat to boiling. Add 25 cc.* of the solution of the material to be examined, prepared so as not to contain more than 0.25 gram of dextrose, and boil for exactly 2 minutes, keeping the beaker covered. Filter immediately through asbestos, and obtain the weight of Cu by one of the procedures given under the Munson and Walker method above. From the Allihn tables determine the corresponding weight of dextrose. The Allihn tables are given in Association of Official Agricultural Chemists: "Methods

* If necessary, the volume of the sugar solution added may be greater or less than 25 cc., provided the volume of water added is correspondingly varied from 60 cc., so that the total volume of sugar solution and water added is always 85 cc.

of Analysis" pages 454–457 (1925); also in Leach: "Food Inspection and Analysis," 4th ed., page 633.

NOTE.—This method may also be used for various other reducing sugars as described below.

Maltose, Lactose, Dextrose.—Use the Munson and Walker general method as described above and calculate from the table the weight of maltose, lactose or dextrose equivalent to the weight of the Cu reduced.

Levulose, Invert Sugar, Arabinose, Xylose, Galactose.—For the determination of these reducing sugars use the Allihn method as described above and multiply the weight of dextrose found in the Allihn tables by the following factors:

Levulose	1.093
Invert sugar	1.044
Arabinose	0.969
Xylose	1.017
Galactose	1.114

REFERENCES.—*U. S. Dept. of Agr., Bur. Chem., Bull.* 107, 241; Leach: "Food Inspection and Analysis;" Association of Official Agricultural Chemists: "Methods of Analysis," 181–196 (1925).

SUCROSE IN SUGAR BEETS

Preparation of Sample.—Pass the sample through a meat grinder fitted with a plate having $\frac{1}{8}$-inch perforations and mix thoroughly.

Alcohol Extraction Method.—Weigh 26 grams of the beet pulp into a 100-cc. Soxhlet flask with about 50 cc. of 90% alcohol and 3–5 cc. of basic lead acetate solution. Connect to a reflux condenser and place on a boiling water bath for 10–15 minutes. Then pour the whole into a Soxhlet extractor, washing out the flask with fresh portions of 90% alcohol. Connect the same flask to the extractor, and fit the latter with a return condenser. Add 90% alcohol until the siphon is started and the flask is about $\frac{3}{4}$ full. Place the flask in a covered water bath kept at a heat that will boil the alcohol freely. Continue the extraction for 1–4 hours, or until the alcohol in the extractor gives no color by the alpha-naphthol test (p. 567).

Remove the flask, transfer the contents to a 100-cc. volumetric flask, cool to standard temperature, dilute to the mark with 90% alcohol, shake and filter, keeping the funnel covered with a watch glass. Polarize in a 200-mm. tube (see pp. 548 and 549).

NOTE.—Avoid evaporation and changes of temperature and also use a minimum amount of basic acetate for clarification, 3 cc. rather than 5 cc. By digesting the beet pulp with alcohol before extraction, the time of extraction is greatly shortened; the pulp becomes thoroughly impregnated with alcohol, and all air is removed, resulting in a good extraction of the whole material. If the pulp is fine and tends to clog the siphon, alcohol-washed cotton may be used as a plug in the extractor before adding the beet pulp, and a fine-mesh screen may be placed over the pulp to keep the whole compact in the extractor.

Hot-water Digestion Method.—Weigh 26 grams of ground beet pulp and transfer with water to a wide-mouthed flask graduated to a content of 201.0 cc. (The additional 1.0 cc. is to allow for the volume of marc and Pb precipitate.) Add 5–10 cc. of basic lead acetate solution and enough water to make the volume 160–170 cc., and shake. Immerse the flask in a water bath at 80° C. and rotate at intervals. At the end of 30 minutes dilute to the mark with water at 80° C. and continue the digestion for 10 minutes longer. Remove the flask from the water bath let cool to standard temperature. Add sufficient conc. acetic acid to make the solution very slightly acid (generally less than 0.5 cc.) and a few drops of ether to break the foam. Apply suction to remove any retained air. Make up to the mark at 20° C., mix thoroughly, filter and polarize in a 400-mm. tube.

REFERENCE.—The above are tentative methods of the Association of Official Agricultural Chemists as published in its "Methods of Analysis," 205 (1925).

SUGAR PRODUCTS

General.—This method includes the usual determinations common to all sugar products, *i.e.*, those in which the main solid ingredient is one or more sugars. For complete analysis of special products see the method for that particular material, *e.g.*, Sugar, Honey, Maple Products, Sucrose in Beets, Fruits, etc.

The methods here given are, unless otherwise specified, the official methods of the Association of Official Agricultural Chemists.

Preparation of Sample.—(*a*) *Liquids* (*molasses, syrups, etc.*).—Mix materials of this class thoroughly. If crystals of sugar are present, dissolve them either by heating gently (avoiding any loss of water by evaporation) or by weighing the whole mass, then adding water, heating until completely dissolved and, after cooling, reweighing. Calculate all results to the weight of the original substance.

(*b*) *Semisolids* (*massecuites, etc.*).—Weigh 50 grams of the sample into a 250-cc. volumetric flask, treat with water, fill to the mark and mix thoroughly; or weigh 50 grams of the sample and dilute with water to 100 grams. If insoluble material remains, mix uniformly by shaking before taking aliquots or weighed portions for the various determinations.

(*c*) *Solids* (*sugar, confectionery, etc.*).—Grind, if necessary, and mix thoroughly to secure uniform samples. In the case of raw sugars, mix thoroughly and as quickly as possible on a glass plate with a spatula, reducing any lumps present with a glass or iron roller; or use a large mortar (dry and clean) and break any lumps with a pestle.

Moisture.—Sugars.—Dry 2–5 grams in a flat dish (nickel, platinum, or aluminum) at the temperature of boiling water for 10 hours; cool in a desiccator and weigh; then dry again for an hour, or until there is not more than 2 mg. change in weight. In the case of coarse-grained sugars, heat at 105–110° C. to expel the last traces of occluded water. Report the percentage loss in weight as Moisture.

Massecuites, Molasses, and Other Liquid and Semi-liquid Products.—(1) *Drying upon Pumice Stone.*—Prepare pumice stone of 2 grades of fineness, one of which will pass through a 1-mm. sieve, the other through a 6-mm. but not a 1-mm. sieve. Digest each with dil. H_2SO_4(1:9) for 8 hours on the steam bath, wash free from acid and heat to dull redness. Make the determination in a flat metallic dish 60 mm. in diameter. Place a layer of the fine pumice stone, 3 mm. in thickness, on the bottom of the dish, then a layer of the coarse pumice stone 6–10 mm. in thickness, dry and weigh. Dilute the sample with a weighed portion of water so that the diluted material shall contain 20–30% of solid matter. Weigh into the dish, prepared as described above, an amount of the diluted sample to yield approximately

1 gram of dry matter. If this weighing cannot be made rapidly, use a weighing bottle provided with a cork through which a pipette passes. Dry at 70° C. under a pressure not exceeding 100 mm. of mercury, making trial weighings at intervals of 2 hours toward the end of the drying period until the change in weight does not exceed 2 mg. For substances containing little or no levulose or other readily decomposable substance, the drying may be made in a water oven at the temperature of boiling water. Report the percentage loss in weight as Moisture.

(2) *Drying upon Quartz Sand.*—Digest pure quartz sand which will pass a 40- but not a 60-mesh sieve with conc. HCl, wash free from acid, dry and ignite. Preserve in a stoppered bottle. Place 25–30 grams of the prepared sand and a short stirring rod in a flat-bottomed dish about 60 mm. in diameter. Dry thoroughly, cool in a desiccator, and weigh. Then add sufficient of the diluted sample to yield about 1 gram of dry matter and mix thoroughly with the sand. Heat on the steam bath for 15–20 minutes, stirring at intervals of 2–3 minutes, or until the mass is too stiff to stir easily. Dry at 70° C. under reduced pressure as in the preceding paragraph. For materials containing no levulose or other readily decomposable substance, dry at atmospheric pressure in a water oven at the temperature of boiling water for 8–10 hours, cool in a desiccator and weigh. Repeat the heating and weighing until the loss of weight in 1 hour is not greater than 0.002 gram. Report the percentage loss in weight as Moisture.

Specific Gravity, Water, and Total Solids.—By Means of a Spindle.—The density of juices, syrups, etc., is most conveniently determined by means of the Brix hydrometer, which is graduated to read directly the percentage by weight of pure sucrose in pure solutions. For rough work, or where less accuracy is desired, the Baumé hydrometer may be used. Use a spindle graduated to tenths and as limited as possible in range of degrees recorded. Have the solution as nearly as practicable of the same temperature as the air at the time of reading, and, if the variation from the temperature of the graduation of the spindle (20° C.) amounts to more than 1°, apply a correction according to Table XXIV. Before taking the density of a juice,

TABLE XXIV—TEMPERATURE CORRECTIONS TO READINGS OF SACCHARIMETERS (STANDARD AT 20° C.)

(This table is calculated from the data on thermal expansion of sugar solutions by Plato, assuming the instrument to be of Jena 16^{111} glass. The table should be used with caution and only for approximate results when the temperature differs much from the standard temperature or from the temperature of the surrounding air)

Temperature ° C.	Observed Percentage of Sugar													
	0	5	10	15	20	25	30	35	40	45	50	55	60	70
	Subtract													
0	0.30	0.49	0.65	0.77	0.89	0.99	1.08	1.16	1.24	1.31	1.37	1.41	1.44	1.49
5	0.36	0.47	0.56	0.65	0.73	0.80	0.86	0.91	0.97	1.01	1.05	1.08	1.10	1.14
10	0.32	0.38	0.43	0.48	0.52	0.57	0.60	0.64	0.67	0.70	0.72	0.74	0.75	0.77
11	0.31	0.35	0.40	0.44	0.48	0.51	0.55	0.58	0.60	0.63	0.65	0.66	0.68	0.70
12	0.29	0.32	0.36	0.40	0.43	0.46	0.50	0.52	0.54	0.56	0.58	0.59	0.60	0.62
13	0.26	0.29	0.32	0.35	0.38	0.41	0.44	0.46	0.48	0.49	0.51	0.52	0.53	0.55
14	0.24	0.26	0.29	0.31	0.34	0.36	0.38	0.40	0.41	0.42	0.44	0.45	0.46	0.47
15	0.20	0.22	0.24	0.26	0.28	0.30	0.32	0.33	0.34	0.36	0.36	0.37	0.38	0.39
15.56*	0.18	0.20	0.22	0.24	0.26	0.28	0.29	0.30	0.30	0.32	0.33	0.33	0.34	0.34
16	0.17	0.18	0.20	0.22	0.23	0.25	0.26	0.27	0.28	0.28	0.29	0.30	0.31	0.32
17	0.13	0.14	0.15	0.16	0.18	0.19	0.20	0.20	0.21	0.21	0.22	0 23	0.23	0.24
17.5	0.11	0.12	0.12	0.14	0.15	0.16	0.16	0.17	0.17	0.18	0.18	0.19	0.19	0.20
18	0.09	0.10	0.10	0.11	0.12	0.13	0.13	0.14	0.14	0.14	0.15	0.15	0.15	0.16
19	0.05	0.05	0.05	0.06	0.06	0.06	0.07	0.07	0.07	0.07	0.08	0.08	0.08	0.08
	Add													
21	0.04	0.05	0.06	0.06	0.06	0.07	0.07	0.07	0.07	0.08	0.08	0.08	0.08	0.09
22	0.10	0.10	0.11	0.12	0.12	0.13	0.14	0.14	0.15	0.15	0.16	0.16	0.16	0.16
23	0.16	0.16	0.17	0.17	0.19	0.20	0.21	0.21	0.22	0.23	0.24	0.24	0.24	0.24
24	0.21	0.22	0.23	0.24	0.26	0.27	0.28	0.29	0.30	0.31	0.32	0.32	0.32	0.32
25	0.27	0.28	0.30	0.31	0.32	0.34	0.35	0.36	0.38	0.38	0.39	0.39	0.40	0.39
26	0.33	0.34	0.36	0.37	0.40	0.40	0.42	0.44	0.46	0.47	0.47	0.48	0.48	0.48
27	0.40	0.41	0.42	0.44	0.46	0.48	0.50	0.52	0.54	0.54	0.55	0.56	0.56	0.56
28	0.46	0.47	0.49	0.51	0.54	0.56	0.58	0.60	0.61	0.62	0.63	0.64	0.64	0.64
29	0.54	0.55	0.56	0.59	0.61	0.63	0.66	0.68	0.70	0.70	0.71	0.72	0.72	0.72
30	0.61	0.62	0.63	0.66	0.68	0.71	0.73	0.76	0.78	0.78	0.79	0.80	0.80	0.81
35	0.99	1.01	1.02	1.06	1.10	1.13	1.16	1.18	1.20	1.21	1.22	1.22	1.23	1.22
40	1.42	1.45	1.47	1.51	1.54	1.57	1.60	1.62	1.64	1.65	1.65	1.65	1.66	1.65
45	1.91	1.94	1.96	2.00	2.03	2.05	2.07	2.09	2.10	2.10	2.10	2.10	2.10	2.08
50	2.46	2.48	2.50	2.53	2.56	2.57	2.58	2.59	2.59	2.58	2.58	2.57	2.56	2.52
55	3.05	3.07	3.09	3.12	3.12	3.12	3.12	3.11	3.10	3.08	3.07	3.05	3.03	2.97
60	3.69	3.72	3.73	3.73	3.72	3.70	3.67	3.65	3.62	3.60	3.57	3.54	3.50	3.43
65	4.4	4.4	4.4	4.4	4.4	4.4	4.3	4.2	4.2	4.1	4.1	4.0	4.0	3.9
70	5.1	5.1	5.1	5.0	5.0	5.0	4.9	4.8	4.8	4.7	4.7	4.6	4.6	4.4
75	6.1	6.0	6.0	5.9	5.8	5.8	5.7	5.6	5.5	5.4	5.4	5.3	5.2	5.0
80	7.1	7.0	7.0	6.9	6.8	6.7	6.6	6.4	6.3	6.2	6.1	6.0	5.9	5.6

* 60° F.

let it stand in the cylinder until all air bubbles have escaped,* and until all fatty or waxy matter has come to the surface and been skimmed off. The cylinder should be large enough in diameter to allow the hydrometer to come to rest without touching the sides. A table for comparison of degrees Brix, degrees Baumé, sp. gr. at 20°/4° C., and sp. gr. at 20°/20° C. is given in Association of Official Agricultural Chemists: "Methods of Analysis," pages 413–423 (1925); and in *Bureau of Standards Circular* 44, page 151 (1918).

If the sample is too dense to determine the gravity directly, dilute a weighed portion with a weighed quantity of water, or dissolve a weighed portion and dilute to a known *volume* with water.

In the first instance the percentage of total solids is calculated by the following formula:

$$\text{Percentage of solids in undiluted material} = \frac{WS}{w},$$

in which S = percentage of solids in diluted material;
W = weight of diluted material;
and w = weight of sample taken for dilution.

When the dilution is made to a definite *volume*, the following formula is to be used:

$$\text{Percentage of solids in the undiluted material} = \frac{VDS}{w},$$

in which V = volume of diluted solution at a given temperature;
D = sp. gr. of diluted solution at same temperature;
S = percentage of solids in diluted solution at same temperature;
and w = weight of sample taken for dilution.

If the spindle reading be made at any other temperature than 20° C., the result should be corrected according to Table XXIV.

By Means of a Pycnometer.

(1) *Specific Gravity at 20°/4° C.*—Determine the sp. gr. of the solution at 20°/4° C. by means of a pycnometer and ascertain the corresponding percentage by weight of sucrose from official tables. When the density of the substance is too high

* Air bubbles may be removed, especially from thick, heavy solutions, by applying suction to the cylinder through a tube passing through a stopper inserted in the top.

for a direct determination, dilute and calculate the sucrose content of the original material as directed above.

Use the following procedure for determining the sp. gr.: Carefully clean the pycnometer by filling with a saturated solution of chromic acid in conc. H_2SO_4, allowing to stand for several hours, emptying, and rinsing thoroughly with water. Fill the pycnometer with recently boiled, distilled water, previously cooled to 16–18° C.; place in a water bath cooled to the same temperature and let the bath warm up slowly to 20° C. Adjust the level of the water to the proper point on the pycnometer; put the perforated cap or stopper in place; remove from the bath; wipe dry with a clean cloth; and, after allowing to stand for 15–20 minutes, weigh. Empty, rinse several times with alcohol and then with ether, remove the ether fumes, allow the pycnometer to become perfectly dry, and weigh. Ascertain the weight of contained water at 20° C. in air (W of the formula below) by subtracting the weight of the empty pycnometer from its weight when full. Cool the sample to 16–18° C., fill the pycnometer with it, bring to 20° C., adjust the level of the liquid to the proper point on the pycnometer, put the perforated cap or stopper in place, wipe dry, and weigh as before. Ascertain the weight of the contained sample at 20° C. in air (S of the formula below) by subtracting the weight of the empty pycnometer from its weight when filled with the sample. Calculate the sp. gr. *in vacuo* by the following formula:

$$G = \frac{S + 0.00105W}{1.00282W},$$

in which G = corrected sp. gr. of sample at 20°/4° C. *in vacuo;*
W = weight of contained water at 20° C. in air;
and S = weight of contained sample at 20° C. in air.

(2) *Specific Gravity at 20°/20°* C.—Determine the sp. gr. at 20°/20° C. with a pycnometer and ascertain the corresponding percentage by weight of sucrose from official tables.

In this case use the following formula for calculating the sp. gr. *in vacuo:*

$$G = \frac{S + 0.00105W}{1.00105W},$$

in which W and S are the same as in the previous formula, and, G = corrected sp. gr. of sample at 20°/20° C. *in vacuo.*

NOTE.—Pycnometer determinations must not be made at any other temperature than those given.

Ash.—METHOD 1.—Heat 5–10 grams of the sample in a 50–100-cc. platinum dish at 100° C. until water is expelled, add a few drops of pure olive oil, and heat slowly over a flame until swelling ceases. Then place the dish in a muffle and heat at low redness until a white ash is obtained. Treat the residue with a little ammonium carbonate solution, re-evaporate, and again heat in the muffle at very dull redness to constant weight.

METHOD 2.—Carbonize 5–10 grams of the sample at a low heat in a 50–100-cc. platinum dish, dissolve the soluble salts in hot water and filter. Burn the filter and residue to a white ash, add the solution of soluble salts, evaporate to dryness at 100° C. and ignite gently. Treat the residue as in Method 1 above.

NOTE.—In the case of impure products it may be advisable to add a few drops of olive oil before carbonizing.

METHOD 3.—SULFATED ASH.—To 5 grams of the sample in a 50–100-cc. platinum dish add 0.5 cc. of conc. H_2SO_4, ignite gently until well carbonized, then burn in a muffle at low redness to constant weight. Express the result as percentage of Sulfated Ash.

Soluble and Insoluble Ash.—Ash the material as directed above under Method 1 or Method 2, add water to the ash in the dish, heat nearly to boiling, filter, and wash with hot water until the combined filtrate and washings are about 60 cc. Return the filter and contents to the dish, ignite carefully, cool, and weigh. Calculate the percentages of water-soluble and water-insoluble ash.

Alkalinity of Soluble Ash.—Cool the filtrate from the above and titrate with 0.1 N HCl and methyl orange. Express the alkalinity as the number of cc. of normal acid per 100 grams of sample.

Alkalinity of Insoluble Ash.—Add an excess of 0.1 N HCl (usually 10–15 cc.) to the ignited insoluble ash in the platinum dish, heat to boiling over an asbestos plate, cool and titrate the excess of HCl with 0.1 N NaOH and methyl orange. Express the alkalinity as above.

Mineral Adulterants in the Ash (Tentative).—Mix 100 grams of the sample with about 35 grams of conc. H_2SO_4 in a large por-

celain evaporating dish and evaporate to a syrupy consistency. Pass an electric current through it while stirring by placing one platinum electrode in the bottom of the dish near one side and attaching the other to the lower end of the glass rod with which the contents are stirred. Begin with a current of about 1 ampere and gradually increase to 4. In 10–15 minutes, the mass is reduced to a fine dry char, which may be readily burnt to a white ash in the original dish over a free flame or in a muffle.

This method is preferred to the ordinary method of heating with H_2SO_4, especially in the case of molasses, because, if properly manipulated, the material comes quietly into the form of a very finely divided char or powder, particularly adapted for subsequent quick ignition.

If an electric current is not available, treat in a large porcelain dish 100 grams of the saccharine solution, evaporate to a syrupy consistency with sufficient conc. H_2SO_4 to thoroughly carbonize the mass, and ignite in the usual manner.

The following adulterants may be present: Salts of Sn, used in molasses to bleach it; mineral pigments, such as $PbCrO_4$ in yellow confectionery; Fe_2O_3, sometimes used to simulate the color of chocolate; and Cu. These elements may be detected by the usual qualitative tests.

Nitrogen.—Determine the nitrogen in 5 grams of the material by the Kjeldahl, Gunning, or Kjeldahl-Gunning-Arnold Method as directed on pages 87–89, using a larger quantity of H_2SO_4, if necessary, for complete digestion.

Sucrose.—Method 1 (Tentative).—(*Substances in which the volume of the combined insoluble matter and precipitate from clarifying agents is less than 1 cc. from 26 grams.*)

Determine sucrose by polarization before and after inversion with HCl as directed on page 548, under Determination of Sucrose in the Absence of Raffinose, paying attention, however, to the footnote.

Method 2.—Use the Chemical Method as described on page 550, determining the reducing sugars by the Munson and Walker method before and after inversion.

Method 3.—Double Dilution Method.—(*Substances in which the volume of the combined insoluble matter and precipitate from clarifying agents is more than 1 cc. from 26 grams.*)

Weigh out a half normal weight (13 grams) of the sample and make up the solution to 100 cc., employing the appropriate clarifier (basic lead acetate for dark-colored confectionery or molasses, and alumina cream for light-colored confectionery). Also weigh out the normal weight (26 grams) of the sample and make up a second solution with the clarifier to 100 cc. Call these solutions *A* and *B*. Filter and obtain direct polariscopic readings of both solutions. Invert each solution with HCl and obtain its invert reading.

The true direct polarization of the sample is equal to four times the direct polarization of *A*, minus the direct polarization of *B*; and the true invert polarization is equal to four times the invert polarization of *A*, minus the invert polarization of *B*. Calculate the sucrose from the true polarizations thus obtained, using the formula on page 549 corresponding to the method used for inversion.

Commercial Glucose (Approximate).—METHOD 1.—(*Substances containing little or no invert sugar.*)—Commercial glucose cannot be determined accurately, owing to the varying amounts of dextrin, maltose, and dextrose which it contains. In syrups, however, in which the amount of invert sugar is so small as not to appreciably affect the result, commercial glucose may be estimated approximately from the polarization by the following formula:

$$G = \frac{(a - S)100}{211},$$

in which G = percentage of commercial glucose solids;
a = direct polarization of normal solution;
and S = percentage of cane sugar.

Express the results in terms of commercial glucose solids polarizing +211° V.*

METHOD 2.—(*Substances containing invert sugar*).—Prepare an inverted half-normal solution of the substance as directed on page 549 under Invert Reading, *except that* after inversion, cool the solution, make neutral to phenolphthalein with NaOH solution, slightly acidify with dil. HCl, and treat with 5-10 cc. of alumina cream before making up to the mark. Filter and

* This result may be recalculated in terms of commercial glucose of any Baumé gravity desired.

polarize at 87° C. in a 200-mm. jacketed metal tube, preferably silver. Multiply the reading by 200 and divide by the factor 196 to express the amount of glucose solids polarizing + 211° V.*

Reducing Sugars.—Determine reducing sugars, either as dextrose or invert sugar, by the Soxhlet method or the Munson and Walker method as described on pages 555 and 551.

Starch (Tentative).—Measure 25 cc. of a solution or uniform mixture, prepared as directed previously under Preparation of Sample, which represents 5 grams of the sample, into a 300-cc. beaker; or, introduce 5 grams of the finely ground sample (previously extracted with ether if it contains much fat) into the beaker; add sufficient water to make the volume 100 cc., heat to about 60° C. (avoiding, if possible, gelatinizing the starch) and let stand for about an hour, stirring frequently to secure complete solution of the sugars. Transfer to a wide-mouthed bottle, rinse the beaker with a little warm water, cool, add an equal volume of 95% alcohol, mix, and let stand at least an hour. Centrifuge until the precipitate is closely packed on the bottom of the bottle and decant the supernatant liquid through a hardened filter. Wash the precipitate with successive 50-cc. portions of 50% alcohol by centrifuging and decanting through the filter until 3 or 4 drops of the washings give no test for sugar with alpha-naphthol when treated as described below. Transfer the residue from the bottle and the hardened filter to a large flask and determine starch by the modified Sachsse method, described on page 618.

Alpha-naphthol Test for Sucrose.—Introduce into a test-tube a few drops of the liquid; add 4 or 5 drops of 20% alcoholic alpha-naphthol solution and 2 cc. of water; shake well, tip the tube and let 2–5 cc. of colorless conc. H_2SO_4 flow down the side. Then hold the tube upright and, if sucrose is present, a color varying from a faint to a deep violet will occur at the junction of the two liquids. On shaking the whole solution becomes a blue-violet color.†

Ether Extract in Confectionery.—Continuous Extraction Method (Tentative).—Measure 25 cc. of a 20% mixture or

* This result may be recalculated in terms of commercial glucose of any Baumé gravity desired.

† This test is suitable for the purpose here specified but it should be remembered that other substances besides sucrose give this color reaction.

solution, prepared as directed previously under Preparation of Sample, into a very thin, readily frangible, glass evaporating shell (Hofmeister Schälchen), or a thin lead or tin-foil dish containing 5–7 grams of freshly ignited asbestos fiber; or if possible to obtain a uniform sample, weigh 5 grams of the mixed finely divided sample into a dish, and wash with water upon the asbestos in the evaporating shell, using, if necessary, a small portion of the asbestos fiber on a stirring rod to transfer the last traces of the sample from the dish to the shell. Dry to constant weight at 100° C., cool, wrap loosely in smooth paper, crush into rather small fragments between the fingers, and transfer carefully the crushed mass, exclusive of the paper, to an extraction tube or a fat-extraction thimble. A thin lead disk (bottle cap) may be substituted for the Schälchen. If a metal dish is used, cut it into small pieces and place in the extraction tube. Extract with anhydrous ether or petroleum ether (b. p. 45–60° C. and without weighable residue) in a continuous extraction apparatus for at least 25 hours. In most cases it is advisable to remove the substance from the extractor after the first 12 hours, grind with sand to a fine powder, and re-extract for the remaining 13 hours. Transfer the extract to a tared flask, evaporate the solvent and dry to constant weight at 100° C.

Roese-Gottlieb Method (Tentative).—Substances such as butter-scotch invariably yield extremely inaccurate results by the above method. In such cases introduce 4 grams of the material, or an amount of a uniform solution equivalent to this amount of the dry substance, into a Röhrig tube or similar apparatus; make up to a volume of 10 cc. with water, add 1.25 cc. of conc. NH_4OH and mix thoroughly. Add 10 cc. of 95% alcohol and mix. Then add 25 cc. of washed ether and shake vigorously for half a minute; finally add 25 cc. of petroleum ether (b. p. below 60° C.), and shake again for half a minute. Let stand 20 minutes, or until the separation of the liquids is complete. Draw off as much as possible of the ether-fat solution (usually 0.5–0.8 cc. will be left) into a weighed flask through a small, rapid filter. (The flask should be weighed with a similar one as a counterpoise.) Again extract the liquid remaining in the tube, this time with 15 cc. each of ether and petroleum ether, shake vigorously half a minute with each, and let settle. Proceed as above, washing the

tip of the spigot and the filter with a few cc. of a mixture of equal parts of the 2 ethers (previously mixed and freed from deposited water). For absolutely exact results the extraction must be repeated. This third extraction usually yields not more than about 1 milligram of fat, if the previous ether-fat solutions have been drawn off closely, or about 0.02% on a 4-gram charge. Evaporate the ether slowly on a steam bath, then dry the fat in a boiling water oven to constant weight.

Test the purity of the fat by dissolving in a little petroleum ether. Should a residue remain, wash the fat out completely with petroleum ether, dry the residue, weigh and deduct the weight.

Paraffin in Confectionery (Tentative).—Add to the ether extract in the flask, as above obtained, 10 cc. of 95% alcohol and 2 cc. of NaOH solution (1:1); connect the flask with a reflux condenser, and heat for 1 hour on the water bath, or until saponification is complete. Remove the condenser and let the flask remain on the bath until the alcohol is evaporated and the residue is dry. Dissolve the residue as completely as possible in about 40 cc. of water and heat on the bath, shaking frequently. Wash into a separatory funnel, cool, and extract with 4 successive portions of petroleum ether, collecting the extracts in a tared flask. Evaporate the petroleum ether and dry to constant weight at 100° C.

Any phytosterol or cholesterol present in the fat would be extracted with the paraffin, but the amount is so insignificant that it may be disregarded generally. The character of the final residue may, however, be confirmed by determining its melting point, sp. gr., and refractive index.

Alcohol in Syrups used in Confectionery ("Brandy Drops").—Collect in a beaker the syrup from a sufficient number of pieces to yield 30–50 grams, strain into a tared beaker and weigh. Introduce the syrup into a 250–300-cc. distilling flask, dilute with half its volume of water, attach the flask to a vertical condenser and distill almost 50 cc., or as much of the liquid as possible without causing charring. Foaming may be prevented by adding a little tannin or a piece of paraffin about the size of a pea to the contents of the distillation flask. Cool the distillate, make up to volume with water, mix well, determine the

sp. gr. of the liquid very carefully with a pycnometer at standard temperature and obtain the corresponding weight of alcohol in the 50 cc. of distillate from standard alcohol tables.* Calculate the percentage by weight of alcohol in the candy filling.

Coloring Matter.—Proceed as under Coloring Matter in Foods (p. 517).

Metals. Proceed as under Metals in Foods (p. 522).

REFERENCE.—Association of Official Agricultural Chemists: "Methods of Analysis" (1925).

HONEY

General.—The Federal Standard for honey (U. S. Department of Agriculture *Circular* 136) requires that it be laevorotatory and contain not over 25% of water, not over 0.25% of ash, and not over 8% of sucrose. The following methods are the official and tentative methods of the Association of Official Agricultural Chemists.†

Preparation of Sample.—(*a*) LIQUID OR STRAINED HONEY.—If the sample is free from granulation, mix thoroughly by stirring or shaking before drawing the weighed portions for analysis. If the honey is granulated, place the container, with the stopper loose, in a water bath, and heat at not over 50° C. until the sugar crystals dissolve; mix thoroughly, cool, and weigh out portions for analysis. If foreign matter is present, such as particles of comb, wax, sticks, bees, etc., heat the sample to 40° C. in a water bath and strain through cheesecloth before weighing.

(*b*) COMB HONEY.—Cut across the top of the comb, if sealed, and separate completely from the comb by straining through a 40-mesh sieve. If portions of the comb or wax pass through the sieve, heat the sample as in (*a*) and strain through a cloth. If the honey is granulated in the comb, heat until the wax is liquefied, stir, cool, remove the wax and take the clear liquid for analysis.

Moisture.—Use the method of Drying upon Quartz Sand as described on page 560, employing an amount of the sample sufficient to give about 1 gram of solids. Add, if necessary, a little

* These tables may be found in Association of Official Agricultural Chemists: "Methods of Analysis," 464–477, (1925); also Leach: "Food Inspection and Analysis," 3d ed., 661–674; and Van Nostrand's "Chemical Annual."

† See its "Methods of Analysis" 199, (1925).

water to incorporate the honey thoroughly with the sand. Dry at 70° C. under a pressure of not over 100 mm. of mercury.

Ash.—Weigh 5–10 grams into a weighed platinum dish, add a few drops of pure olive oil to prevent spattering, heat carefully till swelling ceases and then ignite to a white ash at not above dull redness.

Soluble and Insoluble Ash.—Add water to the ash in the platinum dish, heat nearly to boiling, filter through an ashless filter paper, and wash with hot water until the combined filtrate and washings measure about 60 cc. Return the filter paper and contents to the dish, ignite carefully, cool, and weigh. Calculate the percentages of water-soluble and water-insoluble ash.

Alkalinity of Soluble Ash.—Cool the filtrate from the above determination and titrate with 0.1 N HCl and methyl orange. Express the alkalinity in terms of cc. of normal acid per 100 grams of the sample.

Polarization.—Direct Polarization.—(*a*) *Immediate Direct Polarization.*—Transfer 26 grams of the honey to a 100-cc. volumetric flask with water, add 5 cc. of alumina cream, dilute to the mark with water at 20° C., filter and polarize immediately in a 200-mm. tube.

(*b*) *Constant Direct Polarization.*—Pour the solution from the tube used in reading (*a*) back into the flask, stopper, and let stand 24 hours, or complete the mutarotation as described on page 548. Then again polarize the solution at 20° C. in a 200-mm. tube.

(*c*) *Mutarotation.*—The difference between (*a*) and (*b*) gives the mutarotation or birotation.

(*d*) *Direct Polarization at 87° C.*—Polarize the solution obtained in (*b*) at 87° C. in a jacketed 200-mm. tube.

Invert Polarization.—(*a*) *At 20° C.*—Invert with HCl 50 cc. of the solution (obtained under Direct Polarization above) as described on page 548 under the Determination of Sucrose in the Absence of Raffinose, and polarize at 20° C. in a 200-mm. tube.

(*b*) *At 87° C.*—Polarize the above solution also at 87° C. in a 200-mm. metal tube, preferably of silver.

Reducing Sugars.—Dilute 10 cc. of the solution used for direct polarization to 250 cc. Pipette out 25 cc. and determine the reducing sugars by the Munson and Walker or the Allihn method

as described on pages 551 and 556 and calculate the result to percentage of invert sugar.

Sucrose.—Take 10 cc. of the solution obtained for invert polarization, dilute with a small amount of water, neutralize with Na_2CO_3, and make up to 250 cc. with water. Pipette 50 cc. of this solution and determine the total sugars as reducing sugars by the Munson and Walker method. Calculate to invert sugar. Deduct the percentage of invert sugar obtained previously and multiply the difference by 0.95. The result is the percentage of sucrose.

Levulose.—Multiply the direct polarization reading at 87° C. by 1.0315 and subtract the product from the constant direct polarization at 20° C.; divide the difference by 2.3919 to obtain the grams of levulose in the normal weight (26 grams) of honey. From this figure calculate the percentage in the original sample.

Dextrose.—Subtract the percentage of levulose above determined from the percentage of invert sugar found under Reducing Sugars, to obtain the approximate percentage of dextrose.

The dextrose can be determined more accurately by multiplying the percentage of levulose by the factor 0.915, which gives its dextrose equivalent in copper reducing power. Subtract this figure from that of the reducing sugars calculated as dextrose, to obtain the percentage of dextrose in the sample.

Note.—Owing to the difference in the reducing powers of different sugars, the sum of the dextrose thus found and the levulose as calculated above will be greater than the total amount of invert sugar obtained under Reducing Sugars.

Dextrin (Approximate).—Transfer 8 grams of the sample (4 grams in the case of dark-colored honey-dew honey) to a 100-cc. volumetric flask (using not more than 4 cc. of water) by letting the sample drain from the weighing dish into the flask and then dissolving the residue in 2 cc. of water. After adding this solution to the contents of the flask, rinse the weighing dish with two 1-cc. portions of water, adding a few cc. of absolute alcohol each time before decanting. Fill the flask to the mark with absolute alcohol, shaking constantly. Set the flask aside until the dextrin has collected on the sides and bottom and the liquid is clear. Decant the clear liquid through a filter paper and wash

the residue in the flask with 10 cc. of 95% alcohol, pouring the washings through the same filter. Dissolve the dextrin in the flask with boiling water and filter through the filter paper already used, receiving the filtrate in a tared dish, prepared as described on page 560, under Drying upon Quartz Sand.

Rinse the flask and wash the filter several times with small portions of hot water, add the washings to the tared dish, and evaporate the whole on a water bath. Dry to constant weight at 70° C. under a pressure not greater than 100 mm. of mercury.

After determining the weight of the alcohol precipitate, dissolve the latter in water and make up to definite volume, using 50 cc. of water for each 0.5 gram of precipitate or part thereof. Determine the reducing sugars in the solution, both before and after inversion, by the Munson and Walker method, expressing results as invert sugar. Calculate the sucrose from the results thus obtained and subtract the sum of the reducing sugars before inversion and of the sucrose from the weight of the total alcohol precipitate to obtain the weight of the dextrin.

Free Acid.—Dissolve 10 grams of honey in water and titrate with 0.1 N NaOH and phenlophthalein. Express results in terms of cc. of 0.1 N NaOH required to neutralize 100 grams of the sample.

Commercial Glucose.—Qualitative Test.—Dilute the honey with an equal volume of water, then add a few cc. of iodine solution (1 gram of iodine, 3 grams of KI, 50 cc. of water). In the presence of commercial glucose the solution turns red or violet, the depth and character of the color depending upon the quality and nature of the glucose employed. A blank test with a pure honey of about the same color should be made in order to secure an accurate color comparison. Should the honey be dark and the percentage of glucose very small, precipitate the dextrin which may be present by adding several volumes of 95% alcohol. Let stand until the precipitate settles (do not filter), decant the liquid, dissolve the residue of dextrin in hot water, cool and apply the above test to this solution. A negative result is not proof of the absence of commercial glucose, as some glucose, especially of high conversion, does not give any reaction with iodine.

Quantitative Determination.—An approximate determination can be made by Browne's formula as follows: Multiply the

difference in the polarizations of the invert solution at 20° C. and at 87° C. by 77 and divide this product by the percentage of invert sugar found after inversion in the sample. Multiply the quotient by 100 and divide the product by 26.7, to obtain the percentage of honey in the sample. 100% minus the percentage of honey gives the percentage of glucose.

Commercial Invert Sugar.—Resorcin Test.—Dissolve 1 gram of resorcin in 100 cc. of conc. HCl. Introduce 10 cc. of a 50% honey solution into a test-tube and add 5 cc. of ether. Shake gently and let stand for some time until the ether layer is clear. Transfer 2 cc. of this clear ether solution to a small test-tube and add a large drop of the fresh resorcin solution. Shake and note the color immediately. In the presence of commercial invert sugar, the resorcin assumes immediately a cherry-red colar. Yellow to salmon shades have no significance.

Feder Aniline Chloride Test.—To 100 cc. of c. p. aniline add 30 cc. of 25% HCl. Introduce 5 grams of the honey into a porcelain dish and add 2.5 cc. of the fresh aniline reagent. A bright orange-red color, turning dark red, indicates the presence of commercial invert sugar. Yellow to salmon shades have no significance.

Note.—The resorcin test may be applied to all types of honey, but the aniline chloride test is of no value in the case of dark-colored honey. When the above tests are positive they can be considered conclusive evidence of the presence of commercial invert sugar in honey, provided the honey has not been stored for some length of time after having been heated to temperatures of 160° F. or more; but negative results are not conclusive evidence of the absence of commercial invert sugar.

Diastase.—Mix 1 part of honey with 2 parts of sterile water. Treat 10 cc. of this solution with 1 cc. of 1% soluble starch solution and digest at 45° C. for an hour. At the end of this time test the mixture with 1 cc. of iodine solution (1 gram of iodine, 2 grams of KI, 300 cc. of water). Treat another 10-cc. portion of the honey solution, mixed with 1 cc. of the soluble starch solution, without heating to 45° C., with the reagent and compare the colors produced. If the original honey had not been heated sufficiently to kill the diastase, an olive-green or brown coloration will be produced in the mixture that has been heated at 45° C. Heated or artificial honey becomes blue.

MAPLE PRODUCTS

General.—The procedures given herewith are the tentative methods of the Association of Official Agricultural Chemists.*

Preparation of Sample.—(A) MAPLE SYRUP.—*For Moisture Determination.*—If the sample contains no crystallized sugar or other sediment, mix thoroughly by shaking. If crystallized sugar is present, redissolve it by heating. If other sediment is present, decant the clear syrup, filtering through cotton wool if necessary.

For Other Determinations.—Transfer about 100 cc. of a uniform mixture of the sample (including any sediment present) to a casserole or beaker, add $\frac{1}{4}$ its volume of water, boil to a temperature of 104° C., and filter hot through a plug of cotton wool. Determine moisture in this prepared sample as directed below and calculate all other determinations to a moisture-free basis.

(B) MAPLE SUGAR, MAPLE PASTE, ETC.—*For Moisture Determination.*—Grind in a mortar, if necessary, and mix thoroughly.

For Other Determinations.—Prepare a syrup by dissolving about 100 grams of the sample in about 150 cc. of hot water, boil to a temperature of 104° C. and filter through cotton wool. Determine moisture in the prepared syrup as directed below and calculate all other determinations to a moisture-free basis.

Moisture.—Use a quantity of the sample, prepared as directed above, sufficient to give about 1 gram of solids, and follow the method for Drying upon Quartz Sand (p. 560).

Polarization.—(A) DIRECT AT 20° C.; (B) INVERT AT 20° C.—Make these determinations as described under the determination of Sucrose in the Absence of Raffinose by Polarization before and after Inversion with HCl (p. 548).

(C) INVERT AT 87° C.—Proceed as described under Commercial Glucose, Method 2 (p. 566).

Reducing Sugars as Invert Sugar.—(A) BEFORE INVERSION.—Proceed as directed on page 551, using the Munson and Walker method. Employ an aliquot of the solution used for the direct polarization (as above) and use only neutral lead acetate for clarification.

(B) AFTER INVERSION.—Proceed as above, using an aliquot of the solution used for the invert polarization.

* "Methods of Analysis" 202 (1925).

Sucrose.—Follow the procedure for Sucrose in Fruits and Fruit Products (p. 585).

Total Ash.—Heat 5 grams of the syrup, prepared as previously described, in a 50–100-cc. platinum dish over a low flame until completely charred. Transfer to a muffle and heat at low redness (not over 550° C.) until a white ash is obtained. If it is difficult to burn off all the carbon, cool the dish and contents, add about 1 cc. of water, evaporate to dryness and return the dish to the muffle. To the cooled ash add about 1 gram of ammonium carbonate, free from non-volatile matter, and 0.5–1.0 cc. of water. Evaporate to dryness, reheat in the muffle for 1–2 minutes, cool in a desiccator and weigh.

Soluble and Insoluble Ash.—See page 564.

Alkalinity of Soluble and Insoluble Ash.—See page 564.

Lead Number (Winton).—Reagent: *Standard Basic Lead Acetate Solution.*—Boil 430 grams of neutral lead acetate and 130 grams of PbO for 30 minutes (or in place of these, 560 grams of Horne's dry basic lead acetate) with 1 liter of water, cool, let settle and dilute the supernatant liquid to sp. gr. 1.25. To a measured amount of this solution add 4 volumes of water and filter if not perfectly clear. The solution should be standardized each time a set of determinations is made.

Determination of Lead in the Blank.—Transfer 25 cc. of the standard basic lead acetate to a 100-cc. volumetric flask, add a few drops of acetic acid and make up to the mark with water. Shake and determine $PbSO_4$ in 10 cc. of the solution, as directed below. The use of the acetic acid is imperative in this case to keep the lead in solution when the reagent is diluted with water.

Determination.—Transfer 25 grams of the sample to a 100-cc. volumetric flask by means of water. Add 25 cc. of the standard basic lead acetate and shake; fill to the mark, shake and let stand for at least 3 hours before filtering. Pipette 10 cc. of the clear filtrate into a 250-cc. beaker, add 40 cc. of water and 1 cc. of conc. H_2SO_4, shake and add 100 cc. of 95% alcohol. Let stand overnight, filter on a weighed Gooch crucible, wash with 95% alcohol, dry in a water oven, and ignite in a muffle or over a Tirrill burner. Apply the heat gradually at first, and if a flame is used, set the Gooch crucible inside of a platinum crucible. Cool and

weigh. Subtract the weight of $PbSO_4$ so found from the weight of $PbSO_4$ found in the blank above and multiply by the factor 27.33. The use of this factor gives the lead number directly without the various calculations otherwise required.

Malic Acid Value (Cowles Method).—Weigh 6.7 grams of the sample into a 200-cc. beaker, add 5 cc. of water, then 2 cc. of a 10% calcium acetate solution and stir. Add gradually, and with constant stirring, 100 cc. of 95% alcohol, and agitate the solution until the precipitate settles; or let stand until the supernatant liquid is clear. Filter off the precipitate and wash with 75 cc. of 85% alcohol. Dry the filter paper and ignite in a platinum dish. Add 10 cc. of 0.1 N HCl and warm gently until all the lime dissolves. Cool and titrate back with 0.1 N NaOH and methyl orange. The difference in cc. divided by 10 represents the malic acid value of the sample. Previous to use the reagents should be tested by a blank determination and any necessary corrections applied.

Metals.—See page 522.

NOTE.—The Federal standard (*U. S. Dept. of Agr. Circ.* 136) requires that maple syrup shall contain not more than 35% of water and shall weigh not less than 11 pounds per gallon of 231 cubic inches.

TOMATO PRODUCTS

General.—Usually the basis of judging the quality of tomato paste products is its bacteriological condition. The U. S. Federal Standards are as follows:

	Maximum
Molds, percentage of fields	66
Yeast and spores in $\frac{1}{60}$ cmm	125
Total bacteria per cc	100,000,000

For certain purposes, however, chemical tests are desirable. The following procedures, unless otherwise indicated, are the official methods of the Association of Official Agricultural Chemists, as published in its "Methods of Analysis," page 220 (1925).

Preparation of Sample.—Shake the unopened container thoroughly to incorporate any sediment, then transfer the entire contents to a large glass or porcelain dish and mix thoroughly, continuing the stirring for at least 1 minute. Transfer the well-

mixed sample to a glass-stoppered container and shake or stir thoroughly each time before removing portions for analysis.

Total Solids (Tentative).—Weigh 5 grams of the sample into a flat-bottomed dish having a diameter of about 6 cm., spread the sample in a thin layer, evaporate to dryness on the steam bath, and dry at 70° C. for 4 hours at a pressure of not over 100 mm. of mercury.

Insoluble Solids (Tentative).—Wash 20 grams of the sample repeatedly with hot water, centrifugalizing after each addition of water and pouring the clear, supernatant liquid through a tared triple filter paper on a Büchner funnel. After 4 or 5 washings transfer the remaining insoluble matter to the filter, dry for 2 hours at 100° C., cool in a desiccator and weigh rapidly. The paper used should be dried previously for 2 hours at 100° C., cooled in a desiccator and weighed. A cylinder, 1–1¼ inches in diameter and 5–6 inches long, is convenient for washing and centrifugalizing.

Soluble Solids (Tentative).—Subtract the percentage of insoluble solids from the total solids to obtain the percentage of soluble solids.

Sand (Tentative).—Weigh 100 grams of the well-mixed sample into a 2–3-liter beaker, nearly fill the beaker with water, and mix the contents thoroughly. Let stand 5 minutes and decant the supernatant liquid into a second beaker. Refill the first with water and again mix the contents. After 5 minutes more decant the second beaker into a third, the first into the second, refill and again mix the first. Continue this operation, decanting from the third beaker into the sink until the lighter material is washed from the sample. Then collect the sand from the 3 beakers on a tared Gooch crucible, dry, ignite and weigh.

NOTE.—Attention is especially called to the fact that under Sand only the figure obtained by this method should be reported. The results obtained by the determination of ash insoluble in HCl are not applicable to the determination of sand, since the sand is so unevenly distributed that reliable results can be obtained only by taking a larger sample than is possible in the determination of ash.

Ash.—Evaporate 10 grams of the sample in a platinum dish to dryness on a water bath and ignite at a low heat not to exceed dull redness. If a carbon-free ash cannot be obtained, exhaust

the charred mass with hot water, filter, burn the insolube matter in the dish till white or nearly so, and then add the filtrate to the ash, evaporate to dryness, heat to low redness till white or grayish white, cool in a desiccator and weigh.

Alkalinity of Ash.—Add to the ash in the platinum dish a measured excess of 0.1 N HCl, warm on the steam bath, cool, add a few drops of methyl orange indicator and titrate the excess of acid with 0.1 N NaOH. Express the alkalinity as the number of cc. of normal acid required to neutralize the ash from 100 grams of the sample.

Sodium Chloride.—Determine Cl either gravimetrically as AgCl or volumetrically by the Volhardt method (p. 584), using a HNO_3 solution of the ash. Calculate the percentage of NaCl.

CALCULATION.—$AgCl \times 0.4078 = NaCl$.

1 cc. 0.1 N $AgNO_3 = 0.005845$ gram NaCl.

Reducing Sugars before Inversion.—Weigh 20 grams of the sample into a 200-cc. volumetric flask, dilute with about 100 cc. of water, clarify with a slight excess of neutral lead acetate solution, dilute to the mark and filter. Remove the excess of Pb with anhydrous $Na_2C_2O_4$ or $K_2C_2O_4$. Filter and determine reducing sugars by the Munson and Walker procedure as described on page 551. Express the result as percentage of invert sugar.

Reducing Sugars after Inversion.—Transfer 50 cc. of the filtrate obtained above to a 100-cc. volumetric flask, add 5 cc. of conc. HCl and let stand overnight. (If the temperature is above 25° C., 10 hours is sufficient.) Nearly neutralize with NaOH solution, cool, dilute to the mark and determine reducing sugars in an aliquot by the Munson and Walker method. Express the result as percentage of invert sugar.

Sucrose.—Deduct the percentage of invert sugar obtained before inversion from that obtained after inversion, and multiply the difference by 0.95. Report the result as Sucrose.

Total Acids.—Dilute 5 grams of the sample with recently boiled and cooled water until it appears very slightly colored (about 250 cc.), and titrate with 0.1 N NaOH and phenolphthalein. Express the result as anhydrous Citric Acid.

CALCULATION.—1 cc. 0.1 N NaOH = 0.0064 gram $H_3C_6H_5O_7$.

Volatile Acids.—Introduce 25 grams of the sample into the inner tube of a modified Sellier distillation apparatus as shown in

Fig. 33. Add a small piece of paraffin to prevent foaming and adjust the tube and its contents in place within the larger flask, which contains about 200 cc. of recently boiled water. Connect the condenser as shown in the figure and distill by heating the outer flask. When about 100 cc. of the distillate have been collected, empty the receiver into a beaker and titrate with 0.1 N NaOH and phenolphthalein. Continue the distillation and titrate each succeeding 10 cc. of distillate until not more than 1 drop of the standard NaOH is required to reach the neutral point. Reserve the neutralized distillate for the detection of butyric acid and calculate the titration to acetic acid.

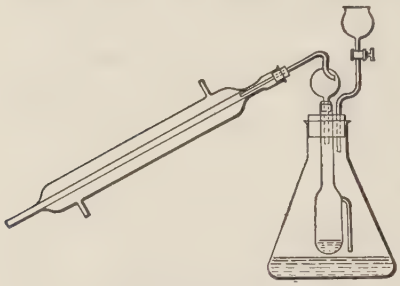


Fig. 33.—Sellier Apparatus for the Determination of Volatile Acids.

Calculation.—1 cc. 0.1 N NaOH = 0.0060 gram acetic acid.

Butyric Acid (Qualitative Test, Tentative).—Evaporate the neutralized distillate, obtained above in the determination of Volatile Acids, to dryness on the steam bath. Decompose the residue with about 5 cc. of 10% H_2SO_4 and note whether the characteristic odor of butyric acid is evolved.

Fixed Acids.—Multiply the percentage of volatile acids by 1.067 and subtract the product from the percentage of total acids to obtain the percentage of fixed acids as citric acid.

FRUITS AND FRUIT PRODUCTS

General.—The following procedures are the official and tentative methods of the Association of Official Agricultural Chemists.

Preparation of Sample.—All samples received in open packages (*i.e.*, not in sterile condition) must be transferred without delay to glass-stoppered containers and kept in a cool place. The determinations of alcohol, total and volatile acids, solids and sugars, particularly in the case of fruit juices and fresh fruits, should be made at once, as fermentation is likely to begin very soon. Portions for determinations of sucrose and reducing sugars may be weighed and, after adding the slight excess of

neutral lead acetate solution required in the determination, may be kept without fermenting for several days if desired. The various products are prepared for analysis as follows:

(*a*) *Juices.*—Mix thoroughly by shaking to insure uniformity in sampling. Remove any extraneous matter by decantation or by filtering through previously washed and dried muslin. Fresh juices may be prepared by pressing the well-pulped fruit in a jelly bag and filtering through muslin. In the case of citrus fruit, express the juice by means of one of the common devices for squeezing oranges or lemons and strain the expressed juice through muslin.

(*b*) *Jellies and Syrups.*—Mix thoroughly to insure uniformity in sampling. Weigh 300 grams into a 2000-cc. volumetric flask and dissolve in water, heating on the steam bath if necessary. Use as little heat as possible to minimize inversion of the sucrose. Cool, dilute to the mark with water, mix thoroughly, and use aliquots for the various determinations. If insoluble material is present, mix thoroughly and filter before removing the aliquots.

(*c*) *Fresh, Canned, or Dried Fruits; Jams, Marmalades, and Preserves.*—Pulp by grinding in a large mortar or by passing through a food chopper and mix thoroughly. Complete this as quickly as possible to avoid loss of moisture. In the case of stone fruits, remove the pits and determine their proportion in a weighed sample. In the case of canned fruits, it is often sufficient merely to examine the syrup in which the fruits are preserved. In such cases separate the liquor by draining and treat as prescribed for juices.

Weigh 300 grams of the well-pulped and mixed sample into a 1.5-2-liter beaker, add about 800 cc. of water and boil for 1 hour, replacing at intervals the water lost by evaporation. Transfer to a 2-liter volumetric flask, cool, dilute to volume, mix and filter.

Alcohol.—Determine the alcohol in 50 grams of the original material as described on page 569 under Alcohol in Syrups used in Confectionery.

Total Solids.—*Juices, Jellies, and Syrups, Containing No Insoluble Matter.*—Proceed as directed on page 559 under Moisture in Massecuites (Drying upon Pumice Stone), employing the sample prepared as directed above under (*a*) or (*b*).

Fresh and Canned Fruits, Jams, Marmalades, and Preserves (Insoluble Matter Present).—Weigh accurately about 20 grams of pulped fresh fruit, or such an amount of fruit products as will give not more than 3–4 grams of dried material, into a large flat-bottomed dish. If necessary to secure a thin layer of the material, add a few cc. of water and mix thoroughly. Dry at 70° C. under a pressure of not over 100 mm. of mercury until consecutive weighings made at intervals of 2 hours do not vary more than 3 mg.

NOTE.—Certain State and Federal regulations require moisture in dried apples to be determined by drying 4 hours at the temperature of boiling water.*

Water-insoluble Solids.—Weigh 25 grams of the prepared sample into a 400-cc. beaker, add 200 cc. of water, cover, heat to boiling, and boil vigorously for 30 minutes, replacing at intervals the water lost by evaporation. Filter the solution through a coarse 15-cm. qualitative filter paper which has been previously dried and weighed in a low-form weighing bottle. Wash the residue and paper with hot water until the washings are colorless and no longer acid to litmus. Dry the paper and residue in the weighing bottle to constant weight at 100–105° C. Calculate the increase in weight to percentage of water-insoluble solids. Save the filtrate and washings for determination of Alcohol Precipitate.

Total Ash.—Determine the ash as follows, using 10 grams of jellies, syrups, preserves, jams, marmalades, and dried fruits; or 25 grams of juices, fresh or canned fruits:

Char the material in a weighed platinum dish and burn until free from carbon at a low heat not exceeding dull redness. If a carbon-free ash cannot be thus obtained, exhaust the charred mass with hot water, collect the insoluble residue on a filter, burn the latter until the ash is white or nearly so, and then cool, add the filtrate to the ash and evaporate to dryness. Heat to low redness until the ash is white or grayish white; cool in a desiccator and weigh.

* For the official method of the Association of Official Agricultural Chemists for determining moisture in dried fruits in general see its "Methods of Analysis," 209 (1925).

If the ash of the water-soluble portion only is desired, evaporate to dryness 100 cc. of the solution prepared as described under Preparation of Sample and then ash as directed.

Alkalinity of Ash.—Into the dish containing the ash introduce a measured excess of 0.1 N HCl, warm on the steam bath, cool, add a few drops of methyl orange indicator and titrate the excess of acid with 0.1 N NaOH. Express the result as the number of cc. of normal acid required to neutralize the ash from 100 grams of the sample. This figure divided by 100 is the Alkalinity Number. Save the titrated solution for the sulfur determination.

Sulfur in Ash.—Add 5 cc. of dil. HCl (1 : 3) to the previous titrated solution; evaporate to dryness and heat for 1 hour at 110° C. to dehydrate any SiO_2. Take up in 5 cc. of dil. HCl (1 : 3), filter and wash the paper thoroughly with hot water. Heat the filtrate to boiling and add, drop by drop, 3 cc. of 10% $BaCl_2$ solution. Evaporate to 100 cc. and let stand overnight. Filter on a weighed Gooch crucible or small quantitative filter paper, wash with hot water until the filtrate is free from Cl, dry, ignite, cool, and weigh as $BaSO_4$. As the amount of precipitate is small, unusual care should be taken in this determination and it should be run in duplicate. Report the result as parts of sulfur per 100,000 parts of the original sample and also as percentage of S in the ash.

CALCULATION.—$BaSO_4 \times 0.1373 = S$.

Total Sulfur.*—In a casserole as large as can be placed in the electric muffle furnace available, place 1–3 grams of MgO (1 gram for fruit juices, 3 grams for heavily sugared products and for dried fruits), 1 gram of powdered sucrose, and 50 cc. of conc. HNO_3. Then add 5–10 grams of the prepared sample. Place the same quantities of the reagents in another casserole for a blank. Evaporate on the steam bath to a pasty consistency. Place the casserole in a cold electric muffle and gradually heat to not above dull redness until all oxides of nitrogen fumes have been driven off. All organic matter will have been destroyed. Cool, dissolve in dil. HCl (1 : 3), and filter. Adjust the acidity so that the solution contains 0.5–1 gram of free HCl, heat to boiling, and add slowly 3 cc. of a 10% $BaCl_2$ solution. Evaporate to 100 cc., let stand overnight, filter, wash, ignite, and weigh as $BaSO_4$.

* For sulfured products and for samples containing little ash.

Correct the result for the $BaSO_4$ obtained in the blank and report as parts of sulfur per 100,000 parts of the original material. The determination should be made in a room free from sulfur fumes.

CALCULATION.—$BaSO_4 \times 0.1373 = S$.

Chlorides.—Ignite a weighed quantity of the sample as directed above under Total Ash. Add a slight excess of dil. HNO_3 (1 : 9), warm on the steam bath, filter and wash thoroughly with hot water. In the combined filtrate and washings determine the Cl either gravimetrically, weighing as AgCl, or by the Volhardt Method of titrating with 0.1 N $AgNO_3$ as follows:

To the solution, somewhat acid with HNO_3, add a measured amount of 0.1 N $AgNO_3$ in slight excess. Stir well, filter and wash the AgCl precipitate thoroughly with cold water. To the combined filtrate and washings add 5 cc. of ferric nitrate indicator solution (p. 12) and titrate the excess of $AgNO_3$ with 0.1 N sulfocyanate solution until a permanent light brown color appears. From the amount of 0.1 N $AgNO_3$ consumed calculate the amount of Cl in the sample.

CALCULATION.—1 cc. 0.1 N $AgNO_3 = 0.00355$ gram Cl.

Total Acidity.—Dilute 10 grams of juice, prepared as directed under Preparation of Sample (*a*), or 25 cc. of the solution prepared as under (*b*) or (*c*), with recently boiled water to about 250 cc., or less if the sample is not highly colored. Titrate with 0.1 N NaOH and phenolphthalein. In the case of highly colored products use azolitmin solution or phenolphthalein powder on a spot plate instead of phenolphthalein solution. Report the results as cc. of normal alkali per 100 grams or 100 cc. of the original material; or calculate the results as malic, citric, or tartaric acid, specifying the acid and expressing results in percentage or in grams per 100 cc.

CALCULATION.—

1 cc. 0.1 N NaOH = 0.0075 gram tartaric acid (anhydrous).
= 0.0067 gram malic acid.
= 0.0064 gram citric acid (anhydrous).

NOTES.—(1) The azolitmin solution should be neutral and of 0.05% strength. Place the azolitmin in the cavities of a spot plate and spot the solution under titration into it. The end-point is reached when the color of the indicator remains unchanged by the addition of a few drops of 0.1 N alkali to the solution under titration.

(2) The phenolphthalein powder is made by mixing 1 part of phenolphthalein with 100 parts of dry, powdered K_2SO_4. Place this indicator in the cavities of a spot plate and flow the solution into it. The end of the titration is indicated when the powder acquires a pink tint.

Volatile Acids.—This determination is seldom required. When necessary it should be conducted according to the procedure described under Volatile Acids in Tomato Products (p. 579), employing 10 grams of the sample, diluted to 25 cc.

Free Mineral Acids.—Use any one of the 3 following methods:

Logwood Method.—Pour 100 cc. of boiling water upon 2 grams of fresh logwood chips, let the infusion stand a few hours and filter. Place several drops of the liquid on a porcelain surface and dry on the water bath. Add to one of the spots a drop of the fruit material to be tested (after concentration if desirable) and evaporate to dryness. A yellow tint remains if free mineral acids are absent, a red tint if they are present.

Methyl Violet Method.—Add 5–10 cc. of water to the fruit product and after mixing well add 4 or 5 drops of methyl violet solution (1 part of Methyl Violet 2B in 10,000 parts of water). A blue or green coloration indicates the presence of free mineral acid.

Quantitative Hehner Method.—To a measured amount of the sample add a measured excess of standard alkali, evaporate to dryness, incinerate and titrate the ash with standard acid and methyl orange. The difference between the number of cc. of alkali first added and the number of cc. of acid needed to titrate the ash represents the free mineral acid present.

Protein.—Determine the nitrogen by the Kjeldahl, Gunning or Kjeldahl-Gunning-Arnold method. Use 5 grams of jelly or other fruit product containing a large amount of sugar, or 10 grams of juice or fresh fruit, and a larger quantity of the H_2SO_4 if necessary for complete digestion. Multiply the percentage of N by 6.25 to obtain the percentage of protein.

Sucrose.—Use either of the following methods:

(*a*) *By Polarization.*—Determine sucrose by polarizing before and after inversion as directed on page 548.

(*b*) *By Reducing Sugars before and after Inversion.*—Clarify with *neutral* lead acetate and determine reducing sugars by the Munson and Walker method (p. 551) and calculate to invert

sugar. Then invert the solution as directed on page 549 (Determination of Sucrose in the Absence of Raffinose by Polarization before and after Inversion with HCl), exactly neutralize the acid and again determine reducing sugars and calculate them to invert sugar from the Munson and Walker table, using the invert sugar column alone. Deduct the percentage of invert sugar obtained before inversion from that obtained after inversion and multiply the difference by 0.95 to obtain the percentage of sucrose. The solutions should be diluted in both determinations so that not more than 240 mg. of invert sugar are present in the amount taken for reduction. It is important that all Pb be removed from the solution with anhydrous powdered $K_2C_2O_4$ or Na_2CO_3 before reduction.

Reducing Sugars.—Determine reducing sugars by the Munson and Walker method as above referred to and express results as invert sugar.

Commercial Glucose.—Follow the procedure for Commercial Glucose in Sugar Products (p. 566), using Method 2.

Dextrin.—Dissolve 10 grams of the sample in a 100-cc. volumetric flask, add 20 mg. of KF and then about $\frac{1}{4}$ of a cake of compressed yeast. Let the fermentation proceed below 25° C. for 2–3 hours to prevent excessive foaming, and then incubate at 27°–30° C. for 5 days. At the end of that time clarify with basic lead acetate solution and alumina cream, make up to 100 cc., filter and polarize in a 200-mm. tube. A pure fruit jelly will show a dextro- or laevo-rotation of not more than a few tenths of a degree. If a polariscope having the Ventzke scale is used and a 10% solution is polarized in a 200-mm. tube, the number of degrees read on the sugar scale of the instrument, multiplied by 0.8755, will give the percentage of dextrin. Or the following formula may be used:

$$\text{Percentage of dextrin} = \frac{C \times 100}{198 \times L \times W};$$

in which C = degrees of circular rotation;
L = length of tube in decimeters;
and W = weight of sample in 1 cc.

Alcohol Precipitate.—To 100 cc. of a 15% solution of jelly or diluted syrup, obtained as under Preparation of Sample above, or

of the washings from the determination of Water-insoluble Solids, add 4–8 grams of sucrose, if sugar is not already present, and evaporate to about 20 cc. If water-insoluble matter separates during evaporation, add more sugar. Cool to room temperature and add slowly, with constant stirring, 200 cc. of 95% alcohol. Let stand at least 1 hour, filter on a 15-cm. qualitative paper and wash with 95% alcohol. Wash the precipitate back into the original beaker with hot water, rinsing the filter paper thoroughly. Evaporate the solution to about 20 cc. and add 5 cc. of dil. HCl (1 :2.5). If water-insoluble matter separates, stir well and warm slightly if necessary to dissolve it. Again precipitate with 200 cc. of 95% alcohol, let stand 1 hour and filter. Wash the precipitate thoroughly with 95% alcohol to remove all HCl. Rinse the precipitate with water from the paper into a platinum dish, evaporate to dryness on the steam bath and dry to constant weight at 100° C. Then ignite and weigh again. Report the loss by ignition as Alcohol Precipitate.

NOTE.—Since the precipitate is often colorless and nearly invisible, care must be taken not to lose any during the operations of dissolving and transferring. If the quantity, as indicated by its volume in the first precipitation, is not excessive, the second filtration may be made through a Gooch crucible containing a thin asbestos mat.

Starch (Qualitative Test).—Dilute a portion of the sample with water, heat nearly to boiling, add several cc. of dil. H_2SO_4 (1 :9) and then $KMnO_4$ solution until all color is destroyed. Starch remains unaffected. Cool and test with dilute iodine solution (blue color). The presence of starch is not necessarily an indication of its addition as an adulterant. It is usually present in small amount in the apple, and occasionally in other fruits, and unless it is found in the fruit product in considerable amount its presence may be due to these natural sources.

Gelatin (Qualitative Test).—The presence of gelatin in jellies and jams is shown by the increased content of nitrogen. Precipitate a concentrated solution of jelly or jam with 10 volumes of absolute alcohol and determine N in the dried precipitate as previously directed under Protein.

Agar-agar (Qualitative Tests).—MICROSCOPIC EXAMINATION.—Heat the jelly with dil. H_2SO_4 (1 :18), add a crystal of $KMnO_4$ and let settle. If agar-agar is present, the sediment will be rich

in diatoms which may be detected by the microscope. The diatoms adhere to the glass and are best obtained by pouring out the liquid, washing the glass with 2 or 3 drops of alcohol and transferring the alcohol to a microscopic slide by means of a glass rod.

By Precipitation.—Cover 30 grams of jam or jelly with 270 cc. of hot water, stir until thoroughly disintegrated and boil for 3 minutes. Filter immediately, while still boiling hot, through a rapid filter paper. In the presence of agar-agar a precipitate will form upon standing not longer than 24 hours. Filter, wash with cold water, and dissolve from the paper with a very small amount of boiling water. Upon chilling this hot water solution a firm jelly will be formed that can be examined by touch. This method will detect 0.2% of agar-agar with certainty if the proportions of jam or jelly and water are strictly observed.

Metals.—Proceed as directed on pages 522–527.

Preservatives.—Proceed as directed on pages 530–541.

Coloring Matters.—Proceed as directed on pages 517–522.

Sweetening Substitutes.—Proceed as directed for Artificial Sweeteners on page 541.

Reference.—Association of Official Agricultural Chemists: "Methods of Analysis," 209-218 (1925).

BUTTER AND BUTTER SUBSTITUTES

(BUTTERINE, OLEOMARGARINE, ETC.)

General.—Butter fat is the fat of milk or butter. It has a peculiar and complex composition, the characteristic constituent being the radicle of butyric acid. Butter consists of a mixture of about 80–90% of butter fat with variable proportions of water, curd and salt. Coloring matter is often added and Na_2CO_3 is sometimes employed to prevent rancidity. In the United States the legal title for all butter substitutes is Oleomargarine (in England and several other countries it is Margarine). In preparing these substitutes various fats are used, including lard and tallow. The proper consistency is often obtained by adding sesame, peanut or cottonseed oil. The fat is then usually incorporated with milk and salt, and colored. Sometimes more or less real butter is added; and palm oil and purified cocoanut oil have also been used.

Preparation of Sample.—If large quantities of butter are to be sampled, use a butter trier or sampler, removing one or more cores from a tub diagonally from top to bottom. Melt completely the portions thus drawn, 100–150 grams, in a closed vessel at as low a temperature as possible and, when melted, shake the whole violently for some minutes, cooling at the same time, until the mass is homogeneous and sufficiently solidified to prevent the separation of the water and fat. Then pour a portion into the vessel from which it is to be weighed for analysis. It should nearly or quite fill the vessel and should be kept in a cool place until analyzed.

Note.—We have found that in some cases the use of a butter trier has a tendency to squeeze moisture out of the butter. It is, therefore, preferable to cut wedges with a knife representative of the tub contents.

It is also very necessary that the final sample, after it has been melted, be shaken thoroughly until it is cold. Otherwise, moisture and salt will settle to the bottom. Our procedure is to collect the sample in a Mason jar provided with a rubber ring and fasten the cover tightly. Place the jar, without opening, in warm water or on the steam bath, agitating at intervals until the sample is completely melted, but avoiding excessive heat. As soon as all the lumps have disappeared place the jar carefully in ice water,* remove it frequently and shake thoroughly until the contents are stiff. Care must be taken that none of the sample solidifies on the sides of the jar until the whole sample is stiff. If such happens, place the jar momentarily in hot water until the solid portions have melted away from the sides. When the sample is stiff enough so that it will flow with difficulty, place the jar in the ice chest until the entire contents become hard. Then open and remove portions for analysis at once.

Moisture.—Weigh accurately 1.5–2.5 grams in a dish with a flat bottom having a surface of at least 20 sq. cm., dry at the temperature of boiling water and weigh hourly until it ceases to lose weight. The use of clean, dry sand or asbestos is permissible.

Fat (Ether Extract).—Indirect Method.—Dissolve in the dish with absolute ether or petroleum ether the dry butter obtained in the moisture determination (in which no absorbent was used), transfer to a weighed Gooch crucible with the aid of a wash bottle filled with the solvent and wash until free from fat. Dry

* To avoid danger of breaking it is safer to place it in cool water first for a few minutes.

the crucible and contents at the temperature of boiling water until the weight is constant and calculate the fat by difference.

Direct Method.—From the dry butter obtained in determining the moisture, either with or without the use of an absorbent, extract the fat with anhydrous, alcohol-free ether, or with petroleum ether (b.p. below 65° C.), receiving the solution in a weighed flask. Evaporate the ether, dry the extract at the temperature of boiling water, and weigh hourly until it ceases to lose weight.

Casein, Ash, and Salt.—Cover the crucible containing the residue from the fat determination by the Indirect Method above and heat, gently at first, gradually raising the temperature to *just below redness.* The cover may then be removed and the heat continued until the contents of the crucible are white. The loss in weight represents casein, and the residue in the crucible mineral matter. Dissolve this mineral matter in water slightly acidulated with HNO_3 and determine chlorine either gravimetrically or volumetrically. Calculate to NaCl.

Salt.—Weigh in a counterpoised beaker 5–10 grams of the sample, add about 20 cc. of hot water and, after the butter is melted, transfer the whole to a separatory funnel. Insert the stopper and shake for a few minutes. Let stand until the fat has all collected on top of the water, then draw off the latter into a flask, being careful to let none of the fat globules escape. Again add hot water to the beaker and repeat the extraction 10–15 times, using each time 10–20 cc. of water. The washings will contain all but a mere trace of the NaCl originally present in the butter. Determine its amount in the whole or an aliquot of the liquid by the volumetric $AgNO_3$ method with K_2CrO_4 as indicator.

Calculation.—1 cc. 0.1 N $AgNO_3 = 0.00585$ gram NaCl.

Examination of Fat.—Preparation of Sample.—Melt the butter and keep it in a dry place at about 60° C. for 2–3 hours, or until the water and curd have entirely separated. Filter the clear, supernatant fat through a dry filter paper in a hot-water funnel or in an oven at about 60° C. Should the filtered liquid fat not be perfectly clear, it must be refiltered.

Reichert-Meissl Number.—Determine the Reichert-Meissl number as described under Animal and Vegetable Oils (p. 319).

Specific Gravity.—Determine with a pycnometer the sp. gr. at 40° C. compared with water at the same temperature.

Notes.—(1) The average Reichert-Meissl number of pure butter fat is 26. To calculate the approximate amount of butter fat in a butter substitute, divide the Reichert-Meissl number of the separated fat by 26 and multiply by the percentage of total fat in the butter substitute.

(2) *U. S. Standards.*—The Federal Standards, as given in *U. S. Dept. of Agr. Circ.* 136, are as follows:

Butter is the clean, non-rancid product made by gathering the fat of milk or cream into a mass, which also contains a small portion of the other milk constituents, with or without salt, and contains not less than 82.5% of butter fat. It may also contain added coloring matter.

Butter Fat is the fat of milk and has a Reichert-Meissl number not less than 24 and a sp. gr. at 40°/40° C. not less than 0.905.

Renovated or Process Butter is made by melting butter and reworking without chemicals or any substances except milk, cream, or salt, and contains not over 16.0% of water and at least 82.5% of butter fat.

Renovated Butter and Oleomargarine.—(*a*) Foam Test (Spoon Test).—Heat 2–3 grams of the sample, either in a spoon or a dish, over a free flame. True butter foams abundantly, whereas process butter will bump and sputter like grease, with little or no foaming. Oleomargarine behaves like process butter, but the chemical tests will determine whether the sample is oleo or butter.

(*b*) Melted Fat Test.—Melt 50-100 grams of the sample at 50° C. The curd from butter will settle, leaving a clear supernatant fat; with renovated butter, the supernatant fat remains more or less turbid.

Coloring Matter.—Pour about 2 grams of the filtered fat, dissolved in ether, into each of 2 test-tubes. Into one of the tubes pour 1–2 cc. of dil. HCl (1:2) and into the other about the same volume of 10% NaOH solution. Shake well and let stand. In the presence of azo dyes, the tube to which the acid has been added will show a pink to wine-red color, while the alkaline solution in the other tube will show no color. If, however, annatto or other vegetable color is present, the alkaline solution will be colored yellow, while no color will appear in the acid solution.

Notes.—(1) For more extensive examination for artificial coloring, see Leach: "Food Inspection and Analysis."

(2) The above methods are those of the Association of Official Agricultural Chemists.

EGGS

General.—Perfectly fresh eggs have been found to show analyses within the following limits:

	Whole Egg		Yolk		White	
	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
Total solids, %.....	26.2	27.2	46.9	50.9	11.8	12.8
Fat (ether extract), %.....	9.3	11.0	24.5	28.8	0.01	0.12
Ammoniacal nitrogen, parts per 100,000.....	1.0	2.0	2.5	3.1	0.0	1.2

The relation of the ammoniacal nitrogen to the fat is a good index for determining the quality of eggs. In Fig. 34 the ammo-

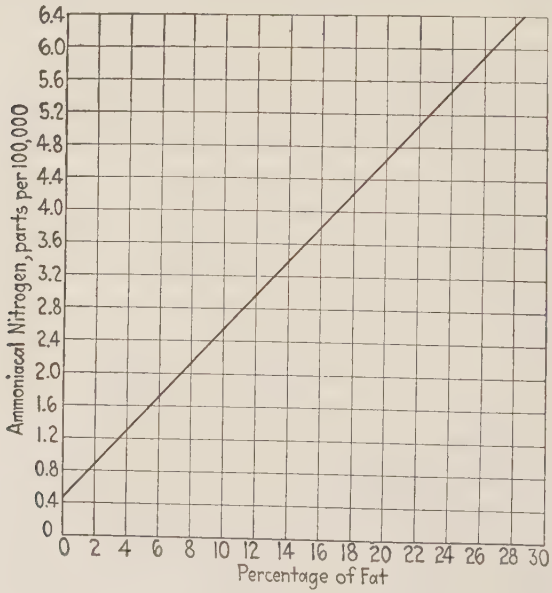


FIG. 34.—Relation of Fat and Ammonical Nitrogen in Eggs.

niacal N in parts per 100,000 is plotted vertically against the fat in percentage horizontally. For edible eggs the intersection

of the horizontal line for ammoniacal N with the vertical line for fat should fall below the heavy diagonal line.

The percentage of fat in a sample of frozen or mixed eggs is also an index of the proportion of the yolks to whites, since the whites are nearly free from fat.

Preparation of Sample.—In the case of frozen eggs keep the sample frozen until ready for analysis and weigh all analytical portions as soon as the sample has melted. If the material is slightly melted around the outside, take the portions for analysis from the inner frozen part. With liquid egg samples stir and mix thoroughly before withdrawing portions for analysis. Make all determinations in duplicate.

Moisture and Fat.—Weigh accurately 5–10 grams of the sample into a tared lead dish $2\frac{1}{2}$–3 inches in diameter or a Hoffmeister schaelchen and dry to constant weight, preferably at 55° C. and under a vacuum of not less than 25 inches. (Calculate the percentage of moisture, if desired.) Then extract the dry residue with absolute ether, using a Knorr apparatus. If this is not available, a Johnson extractor may be used.

If a tared lead dish is used, cut through the sides at 4 equidistant points and roll between 2 fat-free filter papers into a cylinder which will fit the extraction tube fairly snugly. If a schaelchen is used, crush it between similar filter papers. Turn in the ends of the cylinder to prevent any solid particles from dropping into the extraction flask. Three hours' extraction is usually sufficient but it should be continued until no more fat is extracted. Distill off the ether and dry the residue to constant weight, preferably at 55° C. in a vacuum of not less than 25 inches. Calculate the percentage of fat in the original sample.

Ammoniacal Nitrogen.—There are 2 general methods for this determination. The nesslerization method is simple and reasonably accurate. It is said not to be quite so accurate as the titration method which is therefore to be preferred in cases of dispute. For eggs containing less than 3.5 parts of ammoniacal N per 100,000, and in ordinary routine work, use the nesslerization method and run the determination in triplicate; otherwise use the titration method.

Nesslerization Method.—*Apparatus.*—The apparatus as shown in Fig. 35 consists of the following: *A*, an acid bottle

containing about 250 cc. of dil. H_2SO_4 (1 :3) to remove any NH_3 from the air-blast entering at *F*; *B*, a tall cylinder about 2×12 inches to contain the sample; and *C*, a 250-cc. volumetric flask containing about 60 cc. of NH_3-free water and 5 cc. of 0.2 N HCl or H_2SO_4 (or its equivalent) to absorb the NH_3. The tubes entering *A* and *B* reach nearly to the bottom and the tube entering *C* reaches below the surface of the liquid and is bulb shaped on the lower end and perforated with small holes. There is a spray trap between *A* and *B* and likewise a trap between *B* and *C*, containing a plug of cotton or glass wool to prevent any foam from passing into *C*. A stopcock at *F* regulates the air blast. Connections are made with glass tubing through 2-hole rubber stoppers.

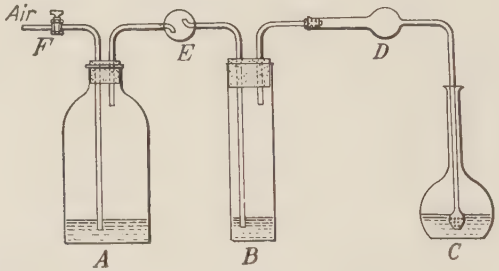


FIG. 35.—Apparatus for Determining Ammonia in Eggs.

Determination.—If the eggs are odorless, weigh out about 25 grams; if the odor is rather strong, weigh about 10 grams. In weighing out the sample pour a sufficient amount of the thoroughly mixed eggs into a beaker and weigh. Then pour the desired amount from the beaker into the cylinder *B* and again weigh. To the eggs in the cylinder add NH_3-free water a little at a time, mixing with the eggs thoroughly after each addition by means of a long rod, using in all an amount of water about equal to the volume of the eggs. Wash off the rod into the cylinder and add to the mixture 5 cc. of a solution of equal parts of a 10% solution of Na_2CO_3 and a 15% solution of $K_2C_2O_4$. The solutions should be made up separately and mixed just before using. Pour in sufficient mineral oil (a very heavy engine oil or a steam-cylinder oil is suitable) to form a layer about $\frac{1}{2}$ inch

deep on the surface of the egg mixture, and connect up the apparatus. Pass through the mixture a current of air sufficiently rapid to cause a slight spray in flask *C*. Continue the aeration for 4 hours or longer (see note 2). If possible the aeration should be accomplished by an air-blast entering at *F*, but if this is not available, suction may be used by fitting the flask *C* with a 2-hole rubber stopper. (In this case a wide-necked flask or bottle will have to be substituted for *C*.)

After air has been blown through the eggs for a sufficient length of time to carry over all the NH_3, remove the flask *C* and make the solution up to 250 cc. Nesslerize an aliquot of this solution and compare it with the regular Nessler standards as used in the determination of NH_3 in sanitary water analysis (p. 675). The aliquot taken for comparison will depend upon the amount of NH_3 present in the eggs. It should not develop a color more intense than that given by 5 cc. of the standard NH_4Cl solution.

The standard NH_4Cl solution contains 0.00001 gram of N per cc. It is made by dissolving 3.822 grams of pure NH_4Cl in 1000 cc. of NH_3-free water, and diluting 10 cc. of this solution to 1000 cc. with NH_3-free water. The Nessler solution is made by dissolving 61.75 grams of KI in 250 cc. of water and adding a saturated solution of $HgCl_2$ cautiously, till a slight, permanent, red precipitate appears. Dissolve this slight precipitate by adding 0.75 gram of powdered KI. Then add 150 grams of KOH dissolved in 250 cc. of water. Make up to 1 liter and let settle overnight.

Carry out the nesslerization in 50-cc. tall Nessler tubes. For the standards take 0.1, 0.3, 0.5, 0.7, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0 cc., respectively, of the above standard NH_4Cl solution, each in a separate tube. In another tube place the aliquot of the solution to be tested. Add 1 cc. of the Nessler solution to each tube and dilute to 50 cc. with NH_3-free water. Mix thoroughly, let stand 10 minutes, and match up the sample with the standard giving the same color. Calculate the amount of ammoniacal N in the original eggs in parts per 100,000.

NOTES.—(1) The Nessler solution described on page 675 may be used in place of the one above described.

(2) *Blank Tests:* It is necessary to run a control blank test, using in place of the egg sample a known amount of the standard NH_4Cl solution

(25 cc. is suitable) and about 25 cc. of the NH_3-free water. The blank test should give at least 95% recovery of the amount of N added. If not, increase the time of aeration both for the blank and for the determination. A separate blank should also be run on the reagents and the NH_3-free water.

TITRATION METHOD.—*Apparatus.*—The apparatus is similar to that described above except that the receiving flask *C* may be conveniently substituted by a wide-mouthed, 8-ounce bottle containing 10 cc. of 0.02 N HCl or H_2SO_4, 2 drops of a saturated solution of methyl red in 95% alcohol, and about 75 cc. of NH_3-free water. (If the sample has a bad odor, use 25 cc. of the 0.02 N acid or reduce the amount of sample employed.)

Determination.—Weigh approximately 25 grams of the eggs into the cylinder *B* as described previously. Add 100 cc. of NH_3-free water and 75 cc. of alcohol, mix well and let stand for 15 minutes. Then add about 1 gram of NaF, 2 cc. of a 50% solution of K_2CO_3 and 1 cc. of kerosene. Immediately connect up the apparatus and aerate for at least 4 hours, using as rapid a current of air as possible. Titrate the excess of acid in *C* with 0.02 N NaOH (free from carbonate) and calculate in terms of parts of ammoniacal N per 100,000 parts of the sample.

CALCULATION.—1 cc. 0.02 N acid = 0.00028 gram N.

NOTES.—(1) If the determination cannot be completed at once, the sample may be left in the cylinder with the alcohol and the NaF overnight, and the K_2CO_3 added just before starting the aeration the next morning.

(2) See note 2 under the Nesslerization Method above.

REFERENCE.—*U. S. Dept. Agr., Bur. Chem., Bull.* 846 (1920).

BAKING POWDERS

General.—This method covers the analysis of mixed baking powders and baking powder ingredients. The following procedures, unless otherwise indicated, are the Official Methods of the Association of Official Agricultural Chemists.

Preparation of Sample.—Remove the entire sample from the package, mix carefully and pass through a 20-mesh sieve.

Total Carbon Dioxide.—REAGENTS.—(*a*) *KOH Solution.*—Dissolve 25 grams in 50 cc. of water.

(*b*) *Soda-lime.*—Finely granulated and freed from dust by sifting.

Apparatus.*—The apparatus as designed by Knorr is shown in Fig. 36. It consists of a flask *A* fitted by means of a ground-glass joint with a glass connection through the upper part of which passes a dropping funnel *B*, and joined at the side with a Liebig condenser *D*. The mouth of the dropping funnel *B* is connected by means of a 1-hole stopper with a soda-lime tube *C*. The upper end of the Liebig condenser is connected by a rubber joint with a Geissler bulb *E*, containing conc. H_2SO_4 for drying the gas passing into the next Geissler bulb *F*, connected with *E*, and containing the strong KOH solution. The bulb *F* is con-

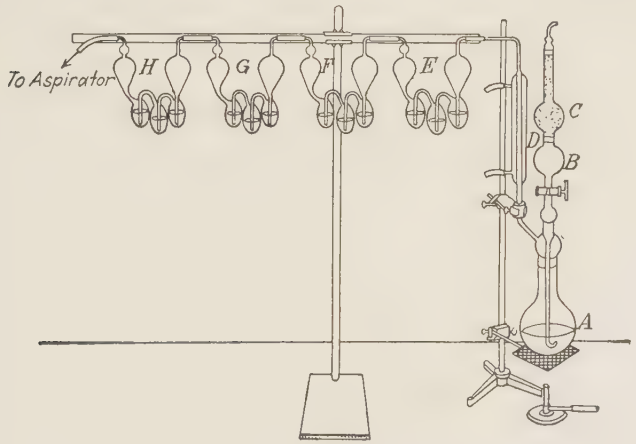


Fig. 36.—Knorr's Apparatus for the Determination of CO_2.

nected with a third Geissler bulb *G*, containing conc. H_2SO_4 for the absorption of moisture escaping from *F*. A fourth Geissler bulb *H* is attached to *G* as a precaution to prevent moisture from the air being absorbed by *G*. *H* is connected with an aspirator. Many analysts prefer to replace the bulb *F* by 2 U-tubes filled with sifted soda-lime.

Determination.—Place 0.5–2 grams of the sample, the amount depending upon the percentage of CO_2 present, in the

* The Association of Official Agricultural Chemists tentatively permits the use of any apparatus based on the absorption principle and giving accurate results when checked with pure $CaCO_3$. In working with Na_2CO_3 or $CaCO_3$ use 0.25–1.00 gram, depending upon the amount of absorbent employed. With baking powders use 0.50–2.00 grams.

flask *A*, which must be perfectly dry. Close the flask with the stopper which carries the funnel tube and the tube connecting with the absorption apparatus. Weigh separately the Geissler bulbs *F* and *G* and attach them to the apparatus. If 2 soda-lime tubes are employed, weigh them separately and refill the first when the second increases materially in weight. Nearly fill the funnel tube *B* with dil. HCl (5 : 4) and place the soda-lime tube *G* in position. Then aspirate air through the Geissler bulbs at a rate of about 2 bubbles per second. Open the stopper of the funnel and let the acid run slowly into the flask, taking care that the evolution of gas is so gradual as not materially to increase the current through the Geissler bulbs. After all the acid has been introduced, close the stop-cock in *B*, continue the aspiration, and heat gradually the contents of the flask to boiling. While the flask is being heated the aspirator tube may be removed, although many analysts prefer, when using ground-glass joints, to aspirate during the entire operation. Continue the boiling for a few minutes after the water has begun to condense in *D*, then remove the flame, open the stop-cock in tube *B* and let the apparatus cool with continued aspiration. Remove the absorption bulbs *F* and *G* and weigh. The increase in weight is due to CO_2.

Residual Carbon Dioxide.—Weigh 2 grams of the sample into a flask suitable for the subsequent determination of CO_2, add 20 cc. of cold water and let stand 20 minutes. Place the flask in a metal drying cell surrounded by boiling water and heat, with occasional shaking, for 20 minutes. To complete the reaction and drive off the last traces of gas from the semisolid mass, heat quickly to boiling and boil for 1 minute. Aspirate until the air in the flask is thoroughly changed, and determine the residual CO_2 by absorption, as directed previously.

Available Carbon Dioxide.—This is obtained by subtracting the residual from the total CO_2. The Federal Standard (*U. S. Dept. Agr. Circ.* 136) requires not less than 12% of available CO_2 in baking powder.

Acidity.*—Dissolve 1 gram in hot water and titrate with 0.1 N NaOH to a permanent pink color to phenolphthalein. Calculate the titration to tartaric acid.

* For cream of tartar and its substitutes; not applicable to $CaH_4(PO_4)_2$.

CALCULATION.—1 cc. 0.1 N NaOH = 0.007502 gram $H_2C_4H_4O_6$.

Free or Combined Tartaric Acid.*—Shake repeatedly about 5 grams of the sample with about 250 cc. of cold water in a flask and let the insoluble portion subside. Decant the solution through a filter and evaporate the filtrate to dryness. Powder the residue, add a few drops of 1% resorcin solution and about 3 cc. of conc. H_2SO_4 and heat slowly. Tartaric acid is indicated by a rose-red color which is discharged on dilution with water.

Total Tartaric Acid.†—Into a 500-cc. porcelain casserole or similar dish weigh 1.881 grams of the sample. Add 10 cc. of water and then 10 cc. of dil. HCl (1:1), adding the latter carefully to avoid loss due to effervescence. Heat gently until most of the starch, if present, is hydrolyzed. Add slowly, with constant stirring, 15 cc. of K_2CO_3 solution containing 328 grams of K_2CO_3 per liter, boil gently on the hot plate for 1 minute and evaporate on the steam bath to incipient crystallization. Remove from the steam bath and add, drop by drop with constant stirring, 3 cc. of glacial acetic acid. Add 2 cc. more of the acetic acid and stir for 3 minutes. Then add 150 cc. of 95% alcohol, carefully rinsing down the sides of the dish with the alcohol, stir vigorously for 5 minutes, and let stand for at least 1 hour. Decant through a Gooch crucible containing a thin layer of paper pulp and wash, mainly by decantation, with 95% alcohol until the combined filtrate and washings measure 550 cc. Test the last few cc. of filtrate with litmus to make sure the precipitate has been properly washed. Return the paper pulp containing part of the precipitate to the residue in the dish and add 120 cc. of hot water. Add 0.2 N NaOH sufficient to neutralize most but not all of the acidity. Boil the solution for 5 minutes and complete the titration with 0.2 N NaOH and phenolphthalein. Twice the number of cc. of 0.2 N NaOH gives the percentage of potassium bitartrate, to which 0.15% must be added to compensate for loss due to solubility in the solutions used. One cc. of 0.2 N NaOH is equivalent to 0.02641 gram of tartaric anhydride $(C_4H_4O_4)_2O_2$; 0.03001 gram of tartaric acid; or 0.03763 gram of $KHC_4H_4O_6$.

Free Tartaric Acid (Qualitative Test).—Extract 5 grams of the sample with absolute alcohol and evaporate the alcohol from the

* Tentative qualitative test, applicable in the presence of phosphates.

† Applicable only in the absence of Ca and Al salts and phosphates.

extract. Dissolve the residue in dil. NH_4OH, transfer to a test-tube, add a good-sized crystal of $AgNO_3$, and heat gently. Tartaric acid is indicated by the formation of a silver mirror. If desired, the absolute alcohol extract may be tested as directed previously under Free or Combined Tartaric Acid.

Starch.—Use method (*a*) for all baking powder ingredients free from lime, and method (*b*) for phosphate, alum phosphate, and all other baking powders containing lime.

(*a*) *Direct Inversion Method.*—Weigh 5 grams of the powder into a 500-cc. volumetric flask. Heat for 2.5 hours with 200 cc. of water and 20 cc. of dil. HCl (5 : 4), using a reflux condenser. Cool and nearly neutralize with NaOH. Dilute to the mark, mix, filter and determine the dextrose in an aliquot of the filtrate by the Munson and Walker or the Allihn method as described on pages 551 and 556. Multiply the percentage of dextrose by 0.90 to get the percentage of starch.

(*b*) *Indirect Method.*—Mix 5 grams of the powder with 200 cc. of dil. HCl (1:11) in a 500-cc. volumetric flask and let the mixture stand for 1 hour, with frequent shaking. Filter on an 11-cm. hardened filter, taking care that a clear filtrate is obtained. Rinse the flask once without attempting to remove all the starch, and wash the paper twice with cold water. Carefully wash the starch from the paper back into the flask with 200 cc. of water. Add 20 cc. of dil. HCl (5 : 4) and proceed as directed above under (*a*).

Note.—The treatment with dil. HCl (1 : 11), without dissolving the starch, removes effectively the lime, which otherwise would be precipitated as tartrate by the alkaline copper solution.

Alum.*—(*a*) *In Baking Powder.*—Ash about 2 grams of the sample in a porcelain dish. Extract with boiling water and filter. Add to the filtrate a few drops of NH_4Cl solution. A flocculent precipitate indicates alum.

(*b*) *In Cream of Tartar.*—Mix about 1 gram of the sample with an equal quantity of Na_2CO_3, burn to ash and proceed as in (*a*).

Analysis of Ash.—(*a*) *Ash Insoluble in Acid.*—Char 5 grams of the sample in a platinum dish at a heat below redness. Boil the carbonaceous mass with dil. HCl (1:3), filter into a 500-cc. volumetric flask and wash with hot water. Return the residue,

* Qualitative test in the presence of phosphates.

together with the paper, to the platinum dish and burn to a white ash. Boil again with dil. HCl, filter, wash, unite the 2 filtrates, dilute to 500 cc. and mix thoroughly. Incinerate the residue after the last filtration and weigh the ash insoluble in acid.

(*b*) *Iron Oxide and Alumina.*—Pipette 100 cc. of the above solution into a 300-cc. beaker. If SiO_2 is present, evaporate to dryness, take up with HCl and filter out the SiO_2. To the acid solution add an excess of Na_2HPO_4 solution and then NH_4OH until a permanent precipitate is obtained. Add conc. HCl drop by drop until the solution is clear. Heat to boiling and boil for 2–3 minutes. Then mix with a considerable excess of 50% $NH_4C_2H_3O_2$ solution and 4 cc. of 80% $HC_2H_3O_2$. Let the precipitate settle, filter and wash with hot water. Dry the precipitate on the filter, remove it as completely as possible from the paper, ignite the paper in a weighed platinum crucible, then add the bulk of the precipitate, ignite strongly, cool in a desiccator and weigh as $FePO_4+AlPO_4$.

Mix the ignited residue with 10 parts of Na_2CO_3 and fuse. Dissolve the fusion in dil. H_2SO_4 (1:6), pass through a Jones reductor and titrate with 0.1 N $KMnO_4$. Calculate the titration to Fe_2O_3.

Calculation.—1 cc. 0.1 N $KMnO_4 = 0.008$ gram Fe_2O_3.

In the same solution after titration determine P_2O_5, either gravimetrically or volumetrically, as described under Phosphoric Acid in Fertilizers. From the weight of the mixed phosphates subtract the weights of P_2O_5 and Fe_2O_3 and report the difference as Al_2O_3.

(*c*) *Lime.*—Heat the combined filtrate and washings from the precipitate of mixed phosphates above to 50° C. and add an excess of saturated $(NH_4)_2C_2O_4$ solution. Let stand in a warm place until the precipitate has settled, filter, wash with hot water, dry and ignite in a platinum crucible, first over a burner and finally over a blast lamp. Cool in a desiccator and weigh as CaO.

Note.—If preferred, the washed CaC_2O_4 may be dissolved in hot dil. H_2SO_4 and titrated with standard $KMnO_4$ solution, as described on p. 697.

(*d*) *Potash and Soda.*—Evaporate 100 cc. of the acid solution of the ash prepared as described above under (*a*) nearly to dryness to remove excess HCl, dilute and heat to boiling. While

still boiling add 10% $BaCl_2$ solution as long as a precipitate forms and then enough saturated $Ba(OH)_2$ solution to make the liquid strongly alkaline. As soon as the precipitate has settled, filter and wash with hot water. Heat the filtrate to boiling, add sufficient ammonium carbonate solution* to precipitate all the Ba, filter and wash with hot water. Evaporate the filtrate to dryness and ignite below redness to remove NH_4 salts. Add to the residue a little water and a few drops of the ammonium carbonate solution. Filter into an unweighed platinum dish, evaporate, ignite below redness, cool in a desiccator and weigh. Digest the residue with hot water, filter through a small filter, wash with hot water, save the filtrate and ignite the filter paper in the same platinum dish. Cool and weigh. The difference between the two weights gives the weight of NaCl+KCl.

Determine K_2O in the filtrate by precipitation as K_2PtCl_6, as described on page 66. Calculate the K_2PtCl_6 to K_2O (reporting as such) and to KCl. Subtract the KCl from the weight of mixed chlorides and calculate the remaining NaCl to Na_2O.

CALCULATIONS.—$K_2PtCl_6 \times 0.1937 = K_2O$.
$K_2PtCl_6 \times 0.3067 = KCl$.
$NaCl \times 0.5303 = Na_2O$.

Phosphoric Anhydride.—Mix 5 grams of the sample with a little $Mg(NO_3)_2$ solution, dry, ignite, dissolve in dil. HCl (1:2.5) and dilute to definite volume. In an aliquot of the solution determine P_2O_5, either gravimetrically or volumetrically, as described under Phosphoric Acid in Fertilizers.

Sulfur Trioxide.—Boil 5 grams of the sample gently for 1.5 hours with a mixture of 300 cc. of water and 15 cc. of conc. HCl. Filter, wash well with hot water, cool the filtrate and washings and dilute to 500 cc. in a volumetric flask. Pipette out 100 cc., dilute to about 200 cc. and to the boiling solution add, drop by drop, an excess of 10% $BaCl_2$ solution. Continue boiling until the $BaSO_4$ settles clear, let stand at least 5 hours, filter on a weighed Gooch crucible, wash with hot water, dry, ignite, cool in a desiccator and weigh as $BaSO_4$ Calculate to SO_3.

CALCULATION.—$BaSO_4 \times 0.3430 = SO_3$.

Ammonia.—Introduce 2 grams of the sample into a 500-cc. distilling flask and add about 350 cc. of water and an excess of conc.

* 1 part of ammonium carbonate to 5 parts dil. NH_4OH (1:2).

NaOH solution. Connect with a vertical condenser and distill into a measured excess of 0.1 N acid. The end of the condenser or an adapter should dip below the surface of the acid. After about 100 cc. have distilled over, titrate the excess of acid in the distillate with 0.1 N NaOH, using methyl red or cochineal as indicator.* Calculate to NH_3.

CALCULATION.—1 cc. 0.1 N acid = 0.001703 gram NH_3.

NOTE.—Ammonia alum is often used as an ingredient of cream of tartar substitutes and baking powders, and ammonium carbonate is occasionally present in baking powders.

1 cc. 0.1 N acid = 0.04533 gram $(NH_4)_2Al_2(SO_4)_4 \cdot 24H_2O$.
= 0.005705 gram $(NH_4)_2CO_3 \cdot H_2O$.

Arsenic (Tentative).—Introduce 5 grams of the sample directly into the apparatus shown on page 54 (Sanger-Black-Gutzeit Method), add 10 cc. of water, a little at a time to prevent frothing over, and then 15 cc. of conc. arsenic-free HCl, drop by drop till frothing ceases. Heat on the steam bath until a drop of the mixture diluted with water and tested with very dil. iodine solution, shows no blue color. Then dilute to about 30 cc. with water, add 4 cc. of 20% KI solution, and proceed as directed under the Sanger-Black-Gutzeit method, Determination (p. 54), beginning with "Heat to about 90° C.," except that the blank and standards for comparison are made by the use of the arsenic-free HCl of the same concentration as that used for the determination.

COCOA, CHOCOLATE, AND CACAO PRODUCTS

General.—Plain or bitter chocolate (chocolate liquor) according to the Federal Standard† is the solid or plastic mass obtained by grinding cacao nibs and contains not less than 50% of cacao fat and, on the moisture- and fat-free basis, not more than 8% of total ash, not more than 0.4% of ash insoluble in HCl and not more than 7% of crude fiber.

By extraction of part of the fat Cocoa is obtained. The fat in cocoa generally runs from 18 to 24%. "Breakfast Cocoa" is required by the Federal Standard to contain at least 22% of cacao fat and sweetened cocoa not more than 65% of sugar in the finished product.

* See p. 89, note 3.
† Effective Jan. 19, 1923.

Sweetened chocolate is made by adding sucrose (and sometimes cocoa butter, spices, etc.) to bitter chocolate, and by the Federal Standard it should contain on the moisture-, sugar- and fat-free basis no higher percentage of total ash, crude fiber, or acid-insoluble ash than is found in the moisture- and fat-free residue of bitter chocolate.

Chocolate is further modified by the addition of milk or milk solids and is sold as Milk Chocolate, either sweetened or unsweetened. According to Food Inspection Decision 136, both sweetened and unsweetened milk chocolates should contain at least 12% of milk solids (for determination see p. 611).

For direct comparison of different kinds of chocolate and cocoa it is best to convert the results of analysis to a "moisture-, fat-, and sugar-free basis." This is accomplished by dividing the analytical figures by $1 - (M + F + S)$, where M, F, and S are the percentages of moisture, fat and sugar, respectively, each expressed as a decimal.

The following procedures where marked Official or Tentative are those of the Association of Official Agricultural Chemists.

Preparation of Sample (Tentative).—Mix powdered products thoroughly and preserve in tightly stoppered bottles. Chill sweet or bitter chocolate until hard and reduce to a finely granular condition by grating or shaving. Mix thoroughly and preserve in a tightly stoppered bottle in a cool place.

Moisture.—Dry 2–5 grams in a flat platinum dish at the temperature of boiling water for 10 hours. Cool in a desiccator and weigh. Then dry again for 1 hour, or until there is only a slight change in weight.

NOTE.—In the case of sweetened chocolate and cocoa it is preferable to use the full 5 grams for moisture and ash determinations.

Ash (Official).—Char the residue from the moisture determination in the platinum dish and burn until free from carbon at not exceeding a dull red heat. If impossible thus to burn the carbon off, exhaust the charred mass with hot water, collecting the insoluble residue on a filter. Burn the residue in the dish until the ash is white or nearly white, and then add the filtrate to the ash and evaporate to dryness. Heat at low redness until the ash is white or grayish white, cool in a desiccator and weigh.

Ash Insoluble in Acid (Official).—Boil the ash above obtained with 25 cc. of dil. HCl (1 : 2.5) for 5 minutes. Filter on a Gooch crucible or ashless filter. Wash with hot water, ignite, cool and weigh.

Soluble and Insoluble Ash (Official).—Ash the material as directed above, employing sufficient sample to contain approximately 1 gram of water-, sugar-, and fat-free material. Add water to the ash, heat nearly to boiling, filter through a quantitative paper and wash with hot water until the combined filtrate and washings measure about 60 cc. Return the filter paper and contents to the platinum dish, ignite carefully, cool and weigh. Calculate the percentages of water-soluble and water-insoluble ash.

Alkalinity of Soluble Ash (Official).—Cool the filtrate from the above and titrate with 0.1 N HCl and methyl orange. Express the alkalinity in terms of the number of cc. of normal acid per 100 grams of sample.

Alkalinity of Insoluble Ash (Official).—Add an excess of 0.1 N HCl (usually 10–15 cc.) to the ignited insoluble ash obtained above in the platinum dish. Heat to boiling over an asbestos plate, cool and titrate the excess of HCl with 0.1 NaOH and methyl orange. Express the alkalinity in terms of cc. of normal acid required per 100 grams of sample.

Total Nitrogen (Official).—Determine nitrogen by the Kjeldahl or Gunning or Kjeldahl-Gunning-Arnold method as described on pages 87–89.

Crude Fiber (Tentative).—Determine crude fiber according to the method on page 527; in cases of dispute use the Official Method.

For the crude-fiber determination employ sufficient sample to contain approximately 1 gram of water-, sugar-, and fat-free material. Both filtrations should be made *upon paper*, the washed fiber either being weighed on a tared filter in the usual way or rinsed from the paper into a tared Gooch crucible, and then dried and weighed.

NOTE.—The residue after the fat extraction may be used directly for crude-fiber determination in the analysis of commercial cocoa and other finely ground or pulverized cacao products. If, however, the material is at all granular, it should be reduced to an impalpable powder, otherwise results will

be much too high. The pulverization may be satisfactorily performed by grinding with ether as described later under the determination of Crude Starch, treating the extracted residue with the hot dil. H_2SO_4 and proceeding from that point in the usual way.

Crude Starch, Direct Acid Hydrolysis (Tentative).*—Weigh 4 grams of the sample, if unsweetened, or 10 grams if sweetened, into a small porcelain mortar, add 25 cc. of ether and grind (see note). After the coarser material has settled, decant the ether, together with the fine suspended matter, upon an 11-cm. paper of sufficiently fine texture to retain the crude starch. Repeat this treatment until no more coarse material remains. After the ether has evaporated from the filter, transfer the fat-free residue to the mortar by means of a jet of cold water and rub to an even paste, filtering on the paper previously employed.† Repeat the process until all the sugar is removed. In the case of sweetened products the filtrate should measure at least 500 cc. With unsweetened material less washing is necessary. Determine the crude starch in the extracted residue as follows:

Wash the residue from the filter into a 500-cc. Erlenmeyer flask with 200 cc. of water. To the solution so prepared, either with sweetened or unsweetened goods, add 20 cc. of dil. HCl (5 : 4) and heat for $2\frac{1}{2}$ hours in the flask with a reflux condenser. Cool and nearly neutralize with NaOH solution. Add 5 cc. of neutral lead acetate solution and dilute to exactly 250 cc. Mix well, filter, and to 100 cc. of the filtrate add sufficient powdered, anhydrous Na_2CO_3 to remove the lead. Shake, let settle, filter through a dry filter and determine reducing sugars in 25 cc. of the filtrate by the Munson and Walker procedure as directed on page 551. The weight of dextrose multiplied by 0.90 gives the weight of crude starch.

NOTE.—If the fat is to be determined, use 3 grams of the residue from the fat extraction (see below) for the starch determination and calculate back to the original sample, correcting also for moisture; *i.e.*, multiply the percentage of starch found in this residue by $1-(M+F)$, where M is the percentage of

* The crude starch by this method will include pentosans and other carbohydrate bodies present which are converted into reducing sugars by HCl. it is consequently higher than the Pure Starch obtained by diastase hydrolysis.

† We have found centrifuging just as satisfactory and much quicker than filtering.

moisture and F is the percentage of fat in the original, each expressed as a decimal.

Pure Starch, Diastase Method (Tentative).—Remove fat and sugar from 4 grams of the material, if unsweetened, and 10 grams if sweetened, as directed under Crude Starch. Wash the wet residue carefully into a 350-cc. beaker with 100 cc. of water, heat over asbestos to boiling with constant stirring, and continue boiling and stirring for 30 minutes. Replace the water lost by evaporation and immerse the beaker in a water bath kept between 55–60° C.; cool to the temperature of the bath, add 20 cc. of freshly prepared malt extract (see notes) and digest the mixture for 2 hours with occasional stirring. Boil again for 30 minutes, dilute, cool, and digest as before with another 20-cc. portion of malt extract. Heat again to boiling, cool, transfer to a 250-cc. volumetric flask, add 3 cc. of alumina cream, make up to the mark and filter through a dry paper. The residue on the paper should show no signs of starch when treated with weak iodine solution and examined microscopically.

Conduct the hydrolysis of 200 cc. of the filtrate by boiling in a flask under a reflux condenser with 20 cc. of dil. HCl (5 : 4) for 2.5 hours and determine the reducing power of an aliquot of the solution as directed under Crude Starch. (Finish the neutralization of the solution with Na_2CO_3 solution and omit the addition of the lead acetate.) Correct for the dextrose due to added malt extract as determined by an accompanying blank analysis upon 20 cc. of malt extract carried through the same procedure. The corrected weight of dextrose, multiplied by 0.90, gives the weight of starch.

Notes.—(1) *Malt Extract.* Digest 10 grams of fresh, finely ground malt for 2–3 hours at room temperature with 200 cc. of water and filter.

(2) Pancreatin and similar powdered preparations, such as Vera Diastase and Panase, obtained from the pancreas of cattle and hogs, are preferable to diastase as starch-converting reagents, since, as a rule, they have no copper-reducing power and hence no correction is necessary. Instead of the malt extract above specified, there may be used the same amount (20 cc.) of a 0.5% aqueous solution of powdered pancreatin, U. S. P.

Fat (Official).—Dry 2 grams (or more) of the sample over conc. H_2SO_4 in a vacuum desiccator until practically all moisture is removed. (Products rich in fat show a tendency to cake at the

temperature of boiling water, hence drying by means of heat must be avoided.) Extract with anhydrous ether in a continuous extractor until no more fat is removed (overnight, if convenient). Grind and repeat the extraction (1–2 hours is generally enough). Evaporate the ether and dry the residue to constant weight at 100° C.

NOTE.—The rapid centrifugal method, though useful and accurate under ordinary conditions, is unreliable during the summer months or in warm latitudes and has not been approved.

Sucrose and Lactose (Tentative).—Transfer 26 grams of the sample to an 8-ounce nursing bottle, add about 100 cc. of petroleum ether and shake for 5 minutes. Centrifugalize until the solvent is clear. Draw off by suction and repeat the treatment with petroleum ether. Place the bottle containing the defatted residue in a warm place until the residual traces of petroleum ether are practically expelled. Add 100 cc. of water, shake until all chocolate is loosened from the sides and bottom of the bottle and then shake for 3 minutes longer. Add basic lead acetate solution from a burette to complete precipitation, then sufficient water to make the total volume of the liquid 110 cc. Mix thoroughly and filter through a folded filter. Make a direct polariscopic reading in a 200-mm. tube at 20° C. Call this A. Precipitate the excess of Pb from solution with anhydrous, powdered $K_2C_2O_4$, a little at a time, avoiding excess. Filter out the precipitate. Introduce 50 cc. of lead-free filtrate into a 100-cc. flask and add 25 cc. of water. Complete the inversion of the solution, as described on page 549 under (*b*) Invert Reading. Obtain the invert reading, multiply by 2 to correct for dilution and call this B.

From the figures obtained calculate the percentages of sucrose (S) and lactose (L) by the following formulas:

$$S=\frac{(A-B)\ (110+x)}{143.0-\frac{t}{2}},$$

and

$$L=\frac{a\left(1.1+\frac{x}{100}\right)-S}{0.79}.$$

In the first formula t is the temperature at which readings were made and x is obtained from the equation:

$$x = \frac{0.2244\ (A - 21d)}{1 - 0.00204\ (A - 21d)},$$

and d in this equation is obtained from

$$d = \frac{A - B}{143.0 - \frac{t}{2}}.$$

NOTE.—In case the determination of sucrose is not desired, the amount of lactose may be determined by the Defren-O'Sullivan Method (see p. 554). In the case of sweetened products the percentage of lactose thus found should be corrected by subtracting 0.7% for invert sugar formed from the sucrose.

Casein in Milk Chocolate (Tentative).—It is unnecessary to defat the chocolate. Weigh 10 grams of the sample into a 500-cc. Erlenmeyer flask and add exactly 250 cc. of 1% $Na_2C_2O_4$ solution. Heat to boiling and boil gently for a few minutes, then cool, add 5 grams of $MgCO_3$ and filter. Determine nitrogen in 50 cc. of this filtrate. Pipette 100 cc. of the filtrate into a 200-cc. volumetric flask and dilute almost to the mark with water. Then precipitate the casein by the addition of 2 cc. of glacial acetic acid or 1 cc. of conc. H_2SO_4. Make to volume, shake, filter, and determine nitrogen in 100 cc. of the filtrate. The difference between the two nitrogen determinations gives the nitrogen derived from the casein, which, multiplied by 6.38, gives the amount of casein present in 2 grams of the sample.

NOTE.—Casein is approximately 80% of the total proteins in milk; hence to find the total milk protein, divide by 0.8 the percentage of casein obtained above.

Caffeine (Decker Method).—Boil 10 grams of the powdered sample and 5 grams of calcined MgO in a flask for 30 minutes with 300 cc. of water; filter by suction on a Büchner funnel, using a round disk of filter paper. Transfer the material and paper to the original flask, add 150 cc. of water, boil for 15 minutes, filter as before, repeat the operation of boiling with 150 cc. of water, and filter. Wash twice with hot water, evaporate the united filtrates (with ignited quartz sand if sugar be present) to complete dryness in a Hoffmeister schälchen, or other suitable thin glass dish of about 300-cc. capacity; grind the dish with contents to a

coarse powder in a mortar; transfer to the inner tube of a Weber extractor,* dry thoroughly in a water oven and extract with $CHCl_3$ for 8 hours in a weighed flask. Distill off the $CHCl_3$ and dry the residue to constant weight at 100° C. Treat the residue in the flask for some hours at room temperature with 50 cc. of pure benzene. Filter through a small paper into a tared dish, evaporate to dryness and dry the caffeine to constant weight at 100° C.

Theobromine (Kunze Method).—Add to the residue on the filter paper from the caffeine determination 150 cc. of water, enough NH_4OH to make the solution slightly alkaline and an excess of 0.1 N $AgNO_3$, accurately measured. Boil to half volume, add 75 cc. of water and repeat the boiling. If any NH_3 remains, repeat the adding of water and boiling until the solution is perfectly neutral. Filter off the insoluble silver theobromine compound and wash with hot water. To the filtrate and washings add 5 cc. of a saturated solution of iron alum and a few cc. of HNO_3 (free from the lower oxides of N). Titrate the excess $AgNO_3$ with 0.1 N KSCN until a permanent light brown color appears. Subtract the amount of $AgNO_3$ thus determined from the original amount added and calculate the difference to theobromine.

Calculation.—1 cc. 0.1 N $AgNO_3 = 0.01801$ gram theobromine.

Other Nitrogenous Substances.—Add the percentages of nitrogen present as theobromine and caffeine, subtract the sum from the percentage of total N and multiply the remainder by 6.25.

Calculations.—Theobromine $\times 0.3111$ = Nitrogen.
Caffeine $\times 0.2887$ = Nitrogen.

Other Nitrogen-free Substances.—To show a complete analysis, subtract from 100% the sum of the percentages of moisture, ash, theobromine, caffeine, other nitrogenous substances, pure starch, and fat, and report the difference as Other Nitrogen-free Substances.

Fat Constants.—Separate the fat in a manner similar to that described above under Sucrose and Lactose, filter the extract through a dry filter, evaporate off the petroleum ether, and determine the melting point, refractive index (at 40° C.), saponi-

* Any other form of extractor which permits of *hot* extraction may be used.

fication number, iodine number and Reichert-Meissl number (see also page 613).

NOTES.—(1) Melting point determinations on this material do not become normal until the fat has been kept for at least 24 hours in a cool place, preferably in a desiccator.

(2) The constants for fat extracted from pure cocoa are given on page 612.

Milk Fat in Milk Chocolate (Tentative).—In the case of milk chocolate the extracted fat will consist of cocoa fat and butter. As the average Reichert-Meissl number of cocoa fat is approximately 0.5 and that of butter fat 26, the approximate percentage of butter fat can be calculated after determining its Reichert-Meissl number. Since, however, the Federal Standard allows a minimum of 24 for the Reichert-Meissl number of butter fat, this figure is used instead of 26 in the calculation.

If A = grams of butter fat in 5 grams of mixed fat,

$B = 5 - A$ = grams of cocoa fat in 5 grams of mixed fat,

and C = Reichert-Meissl number of extracted fat;

then $$C = \frac{24A + 0.5B}{5} = \frac{23.5A + 2.5}{5},$$

and $$A = \frac{C - 0.5}{4.7}.$$

Whence, percentage butter fat = percentage total fat $\times \frac{C - 0.5}{23.5}$.

Milk Solids in Milk Cocoa or Chocolate.—The milk solids are calculated as the sum of the butter fat, total milk proteins, lactose, and milk ash. The amount of milk ash is calculated by taking 5%* of the sum of the butter fat, milk proteins, and lactose.

As a check on the above calculations, it may be noted that the average composition of milk solids is approximately as follows:

	Per cent
Total protein	29.9
Lactose	35.5
Butter fat	28.4
Ash	5.5
Citric acid	0.7
	100.0
Casein	23.7

* According to Leach: "Food Inspection and Analysis," this would be 5.9%, but the Food Laboratories of the U. S. Dept. of Agriculture use 5%

References.—Association of Official Agricultural Chemists: "Methods of Analysis," 43 (1925); Leach: "Food Inspection and Analysis."

COCOA BUTTER

General.—Cocoa Butter (or more properly Cacao Butter) is the fat of the cacao bean. The beans are chiefly used for the preparation of cocoa and chocolate products, so that cocoa butter is largely the byproduct of this industry. The proportion of fat in the beans generally varies from 50–56%.

Cocoa butter has a yellowish-white color which turns white on keeping. It has the pleasant odor of chocolate. The acid number of fresh butter ranges from 1–2 (free fatty acid, calculated as oleic acid, 0.5–1.0%). The constants of pure cocoa butter are generally given as follows:

Sp. gr. at 15.5°/15.5° C	0.950–0.976
Melting point	28–35° C.
Refractive index at 40° C	1.4565–1.4598
Iodine number	32–42
Reichert-Meissl number	0.2–0.8
Saponification number	192–202

The Federal Standard (*Circ.* No. 19) for edible cocoa butter requires that it shall not be rancid; shall have a refractive index at 40° C. of 1.4566–1.4598; iodine number of 33–38; and melting point of 30–35° C.

Cocoa butter is frequently adulterated and sometimes wholly substituted by stearin of cocoanut and palm nut oils. These are readily differentiated from cocoa butter by their low iodine number (4–6 for cocoanut stearin) and their Reichert-Meissl number (generally 3.2–6.3 for stearins).

Analysis.—The determinations of Sp. Gr., Melting Point, Refractive Index, Iodine Number, Reichert-Meissl Number, and Saponification Number are described under Animal and Vegetable Oils.

Notes.—(1) Freshly melted cocoa butter shows a considerably lower melting point than the normal one and only regains its normal (higher) melting point when the sample has been at least 24 hours, preferably several days, in a cool place in a desiccator.

(2) The sp. gr. of solid cocoa butter which has been melted does not become normal for some time, often several days. It is preferable, therefore, to take the sp. gr. of the melted fat as compared with water at 15° C.

Whymper* gives the sp. gr. at 50°/50° C. as 0.8921 and the temperature correction as 0.000717 per °C. This makes the sp. gr. at 30°/15° C. 0.9065. It is not possible to determine the sp. gr. at an elevated temperature and correct to 15° C., as the correction coefficient does not hold when the material changes from liquid to solid.

Cocoa Butter Substitutes.—It is difficult to detect adulterants in cocoa butter when they are present in small amounts (5–10%) simply by interpretation of the fat constants. Some of the substitutes, moreover, especially hydrogenated cottonseed oil, have constants so near those of cocoa butter that it is practically impossible to detect their presence by this procedure. For a given strength of glacial acetic acid the critical temperature of dissolution of a given cocoa butter is constant within 1° C. Pure cocoa butter is also soluble in a mixture of acetone and CCl_4. The following two methods have been adopted as tentative by the Association of Official Agricultural Chemists.†

Critical Temperature of Dissolution in Acetic Acid.—*Apparatus.*—Insert a thermometer reading to 0.1° C. into a cork that fits a $6\times\frac{3}{4}$-inch test-tube. The thermometer should extend far enough into the tube so that the bulb will be covered by 10 cc. of liquid. Place the tube in a larger tube $4\times1\frac{1}{4}$ inches containing glycerine, and hold firmly in place with a cork having a groove cut in the side to equalize the pressure when heat is applied.

Determination.—Filter a portion of the sample through a dry filter paper in an oven at about 110° C. to remove traces of moisture. Let the filtered sample cool until barely warm and weigh (to the second decimal place) 5 grams of the sample and 5 grams of glacial acetic acid (99.5%) into the test-tube. Insert the cork with the thermometer and place the test-tube in the glycerine bath. Heat and shake frequently until a clear solution is obtained. Let the solution cool with constant shaking without removing from the glycerine bath. Note the temperature at which the first sign of turbidity appears. Make a similar test with the same acetic acid on a sample of pure cocoa butter.

Correction Factor.—Free fatty acids lower the turbidity temperature. A correction must therefore be made for the acid

* "Cocoa and Chocolate; Their Chemistry and Manufacture."

† See its *Journal*, **6**, 278 (1923).

number of the sample. If the strength of the acetic acid is such that the turbidity temperature of pure cocoa butter is approximately 90° C., one unit of acid number will cause a reduction of 1.4° C. in the critical temperature of dissolution. If the turbidity temperature is approximately 100° C., one unit of acid number will cause a reduction of 1.2° C. For intermediate temperatures the reduction is proportional.

Determine the acid number of both the sample and the pure cocoa butter, as described on page 311. Multiply the acid number by the correction factor, and add the result to the observed turbidity temperature. The figure obtained is the true Critical Temperature of Dissolution. If the result obtained on the sample is lower by more than 2° C. than that of the pure cocoa butter, adulteration with cocoanut, palm kernel, corn, peanut, cottonseed oils, or their stearins, or other vegetable oils is indicated.

NOTE.—Using acetic acid with which pure cocoa butter gives a critical temperature of 96° C. it has been found that the following temperatures are given by various substitutes:

Shell butter	71° C.
Cocoanut and palm kernel products	16° C.
Hydrogenated cottonseed oil	104° C.
Tallow	94° C.
Corn oil	20° C.
Cottonseed oil	46° C.
Olive oil	63° C.
Peanut oil	52° C.
Sesame oil	40° C.

Mixtures of any of these products with pure cocoa butter change the critical temperature of dissolution by an amount approximately proportional to the amount of substitute used. The only substitutes in use which have a critical temperature as high as pure cocoa butter are hydrogenated oils and tallow. These adulterants may be detected by the solubility test below.

ACETONE-CARBON TETRACHLORIDE TEST.—Dissolve 5 cc. of the warm fat, previously filtered through a dry filter in an oven at about 110° C. to remove traces of moisture, and 5 cc. of a mixture of equal volumes of acetone and CCl_4 in a test-tube. Let the solution stand in ice water for 20–30 minutes. Run a blank on a sample of pure cocoa butter at the same time. If hydrogenated oil, tallow, oleostearin, or paraffin is present, a white

flocculent precipitate will soon appear. If the water is cold enough, cocoa butter may solidify. If a precipitate forms, remove the sample from the ice water and let it remain at room temperature for a time. Solidified cocoa butter will soon melt and go into solution, but if the precipitate is due to any of the above-mentioned possible adulterants, a much longer time will be required.

REFERENCE.—Lewkowitsch: "Chemical Technology and Analysis of Oils, Fats and Waxes," **2,** 475.

FEED STUFFS AND MIXED GRAINS

Preparation of Sample.—Grind the sample so that it will pass through a sieve having circular holes 1 mm. in diameter and mix thoroughly. This is very important in the case of mixed grains. A suitable mill is the grinding and pulverizing mill 059 made by the Enterprise Manufacturing Company, Philadelphia. The mill should be screwed down tightly and so-called spice grinders used in it. Pass the material through the mill, sieve it on the millimeter sieve, and regrind the residue until it all passes the sieve. If it is impossible to grind it fine enough to go through the sieve, pound up the residue in an iron mortar. Finally mix the ground sample very thoroughly before removing portions for analysis.

In the case of soft or sticky feeds that cannot be ground, reduce the sample to as fine a state as possible.

NOTE.—For occasional samples the No. 0 mill is satisfactory, although this is not made to run by power. The Bureau of Chemistry at Washington uses the Enterprise Mill, serial 2962, which is run by a $\frac{3}{4}$-horsepower motor.

Moisture.—Dry a portion of the ground material, representing about 2 grams of dry substance, at the temperature of boiling water to constant weight (approximately 5 hours) under a pressure of not over 100 mm. of mercury. Or, dry in a current of dry hydrogen at the same temperature but at atmospheric pressure. If the substance is in a glass vessel the latter should not be in contact with the boiling water. Report the percentage loss in weight as Moisture.

Ash.—Weigh the equivalent of about 2 grams of the dry material, char in a weighed platinum dish and burn until free

from carbon at the lowest possible heat (not above dull redness). If a carbon-free ash cannot be obtained in this manner, exhaust the charred mass with hot water, collect the insoluble residue on a filter, ignite it in the dish until the ash is white or nearly so, then add the filtrate to the ash in the dish and evaporate to dryness. Heat the whole at low redness till the ash is white or grayish white, cool in a desiccator and weigh.

Crude Protein.—Determine the nitrogen by the Kjeldahl, Gunning or Kjeldahl-Gunning-Arnold method, as described on pages 87–89. Multiply the percentage of N by 6.25 to obtain crude protein.

Albuminoid Nitrogen.—Stutzer's Reagent.—Dissolve 100 grams of pure copper sulfate in 5 liters of water, add 2.5 cc. of glycerol and then 10% NaOH solution until the liquid is just alkaline. Filter, rub the precipitate in a mortar with water containing 5 cc. of glycerol per liter, and wash by decantation or filtration until the washings are no longer alkaline. Rub the precipitate up again in a mortar with water containing 10% of glycerol, thus preparing a uniform gelatinous mass that can be measured with a pipette. Determine approximately the quantity of $Cu(OH)_2$ in 5 cc. of this mixture by diluting to 50 cc. with water, filtering, washing, igniting, and weighing as CuO. Multiply the weight of CuO by 1.23 for the weight of $Cu(OH)_2$.

Determination.—Place 0.7 gram of the sample in a beaker, add 100 cc. of water and heat to boiling; or, in case of substances rich in starch, heat on the water bath for 10 minutes. Add a quantity of the Stutzer's reagent containing about 0.5 gram of the $Cu(OH)_2$, stir thoroughly, filter when cold, wash with cold water and, without removing the precipitate from the filter, determine the nitrogen according to the Kjeldahl, Gunning, or Kjeldahl-Gunning-Arnold method, as described on pages 87–89, adding sufficient K_2S or Na_2S solution to precipitate all of the Cu and Hg. The filter paper used must be essentially free from N.

If the material (such as seeds, seed residue, or oil cake) is rich in alkaline phosphates, add 1–2 cc. of a 10% solution of potash or soda alum, free from NH_3, then the $Cu(OH)_2$ and mix well by stirring. If this is not done, copper phosphate and free alkali may be formed and the protein-copper precipitate partially dissolved in the alkaline liquid.

Amido Nitrogen.—Subtract the percentage of albuminoid N from the total N to obtain the amido N.

Crude Fat (Ether Extract).—Direct Method.—*Reagent.*—Prepare anhydrous ether as follows: Wash the commercial ether with 2–3 successive portions of water. Add solid NaOH or KOH and let stand until most of the water has been absorbed. Decant into a dry bottle. Add carefully cleaned metallic sodium cut into small pieces and let stand until there is no further evolution of hydrogen. Keep the ether, thus dehydrated, over metallic Na in a loosely stoppered bottle to allow any accumulated H_2 to escape. It may be drawn off with a pipette as required.

Determination.—Large quantities of soluble carbohydrates may interfere with the complete extraction of the fat. In such cases extract with water before proceeding with the determination. Extract about 2 grams of the material, dried as previously described, with the anhydrous ether for 16 hours. Dry the extract at the temperature of boiling water for 30 minutes, cool in a desiccator and weigh. Continue the alternate drying and weighing at 30-minute intervals to constant weight. For most feeds a period of 1–1.5 hours is required.

Indirect Method.—Determine the moisture as previously directed, then extract the dried substance for 16 hours with anhydrous ether, dry again and report the percentage loss in weight as Ether Extract.

Crude Fiber.—Determine Crude Fiber as directed on page 527.

Carbohydrates.—In feed stuffs, free from sugar, and in mixed grains the carbohydrates are generally taken by difference. Add together the percentages of moisture, ash, protein, fat, and crude fiber and subtract the sum from 100% for the carbohydrates.

Total Sugars.*—Preparation of Solution.—Place 10 grams of the sample in a 250-cc. volumetric flask. If the substance has an acid reaction, add 1–3 grams of $CaCO_3$. Boil on a steam bath for 1 hour with 125 cc. of 50% alcohol by volume, using a small funnel in the neck of the flask to condense the vapor. Cool and let stand several hours, preferably overnight. Make up to volume with neutral 95% alcohol, mix thoroughly, let settle, pipette 200 cc. into a beaker and evaporate on the steam bath to a volume of 20–30 cc. Do not evaporate to dryness; a little

* Particularly applicable to cattle feeds.

alcohol in the residue does no harm. Transfer to a 100-cc. volumetric flask and rinse the beaker thoroughly with water, adding the rinsings to the contents of the flask. Add enough saturated neutral lead acetate solution to produce a flocculent precipitate, shake thoroughly and let stand 15 minutes. Make up to the mark with water, mix thoroughly and filter through a dry filter. Add sufficient anhydrous Na_2CO_3 or $K_2C_2O_4$ to the filtrate to precipitate all the Pb. Again filter through a dry filter and test the filtrate with a little of the precipitant to make sure that all the Pb has been removed.

Reducing Sugars.—Determine the reducing sugars by the Munson and Walker method (see p. 551), employing the Soxhlet modification of Fehling's solution and using 25 cc. of the solution prepared as above directed (representing 2 grams of the sample). Express the results as Dextrose or as Invert Sugar. (See note.)

Sucrose.—Introduce 50 cc. of the solution prepared as above directed into a 100-cc. volumetric flask; add a piece of litmus paper, neutralize with HCl, add 5 cc. of conc. HCl and let the inversion proceed at room temperature (for 24 hours at a temperature of 20–25° C. or for 10 hours, if the temperature is above 25° C.). When inversion is complete, transfer the solution to a beaker. Neutralize with Na_2CO_3, return the solution to the 100-cc. flask, dilute to the mark with water, filter if necessary and determine reducing sugars in 50 cc. of the solution (representing 2 grams of the sample), as directed above under Reducing Sugars. Calculate the result as invert sugar. Subtract the percentage of reducing sugars before inversion from the percentage of total sugar after inversion, both calculated as invert sugar, and multiply the difference by 0.95 to obtain the percentage of sucrose present.

Note.—Since the insoluble material of grain or cattle food occupies some space in the flask as originally made up, it is necessary to correct for this volume. Results of a large number of determinations on various materials have shown the average volume of 10 grams of material to be 7.5 cc., and, therefore, to obtain the true amount of sugars present all results must be multiplied by the factor 0.97 (since 7.5 cc. is 3% of 250 cc.).

Starch.—Direct Acid Hydrolysis (Modified Sachsse Method).*—Stir a weighed quantity of the sample representing

* By this method there will be included as starch the pentosans and other carbohydrate bodies present which undergo hydrolysis and inversion to reducing sugars on boiling with HCl.

2.5–3 grams of the dry material in a beaker with 50 cc. of cold water for 1 hour. Transfer to a filter and wash with 250 cc. of cold water. Heat the insoluble residue for 2.5 hours with 200 cc. of water and 20 cc. of dil. HCl (5 : 4) in a flask provided with a reflux condenser. Cool and nearly neutralize with NaOH. Add the proper clarifying agent and complete the volume to 250 cc. Filter and determine the dextrose in an aliquot of the filtrate as directed by the Munson and Walker method (p. 551) or the Allihn method (p. 556). The weight of dextrose obtained, multiplied by 0.90, gives the weight of starch.

NOTE.—The factor 0.90 is the theoretical ratio between starch and dextrose but, according to Noyes and other investigators, the factor 0.93 more nearly approaches the actual yield.

DIASTASE METHOD.—*Malt Extract.**—Digest 10 grams of fresh, finely ground malt for 2–3 hours at ordinary temperature with 200 cc. of water and filter. Determine the quantity of dextrose in a given volume of the filtrate after boiling with acid, etc., as in the starch determination, and make the proper correction in the subsequent determination.

Determination.—Extract a convenient quantity of the substance (ground to an impalpable powder and representing 4–5 grams of the dry material) on a hardened filter with 5 successive portions of 10 cc. of ether, wash with 150 cc. of alcohol (10% by volume) and then with a few cc. of 95% alcohol. Place the residue in a beaker with 50 cc. of water, immerse the beaker in boiling water, and stir constantly for 15 minutes, or until all the starch is gelatinized. Cool to 55° C., add 20 cc. of the malt extract, and maintain at this temperature for 1 hour. Heat again to boiling for a few minutes, cool to 55° C., add 20 cc. of the malt extract, and maintain at this temperature for 1 hour, or until the residue treated with iodine solution shows no blue color upon microscopical examination. Cool, make up directly to 250 cc. and filter. Place 200 cc. of the filtrate in a flask, add 20 cc. of dil. HCl (5:4), connect with a reflux condenser, and heat in a boiling water bath for 2.5 hours. Cool, nearly neutralize with 10% NaOH solution, finish the neutralization with Na_2CO_3 solution, and dilute to 500 cc. Mix the solution thoroughly, pour through a dry filter, and determine the dextrose in an

* See also note 2 on p. 607.

aliquot by the Munson and Walker or the Allihn method. Conduct a blank determination upon the same volume of the malt extract as used with the sample and correct the weight of dextrose accordingly. The weight of the dextrose obtained, multiplied by 0.90, gives the weight of starch.

Pentosans.—Weigh 2–5 grams of the sample, using such an amount that the weight of phloroglucide obtained shall not exceed 0.300 gram, and follow the procedure described under Furfural Value of Cotton Cellulose (p. 493).

Galactan.—The determination of galactan is seldom required. The tentative method of the Association of Official Agricultural Chemists is given in its "Methods of Analysis," page 121 (1925).

Water-soluble Acidity (Tentative).—Weigh 10 grams of the sample into a shaking bottle. Add 200 cc. of water and shake for 15 minutes. Filter the extract through a folded filter, pipette out 20 cc. (equivalent to 1 gram), dilute with 50 cc. of water and titrate with 0.1 N NaOH and phenolphthalein. Report results in terms of cc. of 0.1 N NaOH required to neutralize 1 gram.

Grit in Poultry Feed.—After thorough mixing, place 2 grams of the ground sample, prepared as previously described, in an evaporating dish of about 30-cc. capacity. Add about 5 cc. of $CHCl_3$ and mix gently with a glass rod so that the liquid comes in contact with all of the sample. Brush the particles adhering to the rod into the dish and, after pushing all particles into the $CHCl_3$ with a 25-mm. circular or square cover-glass, use the latter to skim off or pull the floating portion of the material over the top of the dish, taking care not to submerge the cover-glass deep enough to disturb the grit settled in the bottom of the dish. After skimming until the surface of the $CHCl_3$ is nearly clear, slowly pour the supernatant liquid into a second evaporating dish, stopping as soon as any grit threatens to pass out.

Now wash the sides of the dish with a few cc. more of $CHCl_3$ and repeat the above operation until no floating particles remain, using the cover-glass as before and pouring off the supernatant liquid. This will require 10–15 cc. of $CHCl_3$. When grit only remains, let the last of the $CHCl_3$ evaporate spontaneously and weigh the residue.

NOTE.—The $CHCl_3$ washings collected in the second dish should be poured out in order to observe whether any grit has been poured into it

during the process. Also examine the residue of grit for impurities. The $CHCl_3$ washings may be saved and recovered by distillation and subsequent drying over $CaCl_2$.

Bone in Meat Scrap.—Use the grit method previously described, except that in some samples it may be found necessary to rub the residue of bone, remaining after the first washing with $CHCl_3$, with a glass rod or small pestle to assist in bringing some of the particles to the surface of the $CHCl_3$.

Salt (Qualitative Test).—Transfer 2 cc. of a 5% $AgNO_3$ solution to a small test-tube of about $\frac{5}{16}$ inch diameter. Carefully add to the liquid an equal volume of the feed, which has been previously ground to pass a 1 mm.-sieve, so that most of the sample floats or remains above the liquid. Gradually incline the tube so that the liquid is absorbed. White patches of AgCl will appear wherever the minutest crystal of salt comes in contact with the liquid.

Reference.—The above are essentially the official methods of the Association of Official Agricultural Chemists (except those marked "Tentative") described in its "Methods of Analysis" 115–122 (1925). There have been slight changes made to conform to the usage of this laboratory.

WHEAT FLOUR

General.—Wheat flour is defined as finely ground and bolted wheat substances. Graham flour is an unbolted wheat meal. The grades of flour commonly made are: (1) Patent flour, forming 85% or less of the flour output; (2) Clear or Bakers' flour, an intermediate grade, inferior to the patent in color and rising properties; (3) Low Grade or "Red Dog" flour, about 5%, suitable only for cattle feed. Some mills make two or more grades of patent and clear. On the other hand, it is also frequent practice to combine all the flour streams other than of low grade to form a so-called "straight" flour.

The byproducts of flour are: (1) Bran, the outer coatings of the grain in flakes; (2) Shorts, the finer offal containing both starchy matter and bran elements; (3) Germ, rich in oil, often run in with the bran. For the composition of typical wheat flours and byproducts, see Leach, "Food Inspection and Analysis," 4th ed., pp. 320–323.

The Federal Standard for flour (U. S. Department of Agriculture *Circ.* No. 136) requires that it shall contain not over 13.5% of

moisture, 1% of ash, and 0.50% of crude fiber, and not less than 1.25% of nitrogen.

The following procedures, with the exception of the tests for alum and ergot, are official and tentative methods of the Association of Official Agricultural Chemists.

Moisture.—Dry approximately 2 grams *in vacuo* at the temperature of boiling water to constant weight (approximately 5 hours). Report the percentage loss in weight as Moisture.

For a routine method which gives results very close to the official, weigh accurately about 2 grams in a tared, covered dish, remove the cover and heat in an air oven at 130° C. (±3°) for 1 hour. Cover the dish while still in the oven, cool in a desiccator for 20 minutes, weigh and calculate the loss in weight as moisture.

Ash.—Weigh 3–5 grams in a shallow platinum dish which has been ignited, cooled in a desiccator, and weighed soon after reaching room temperature. Burn in a muffle until the ash is light gray, or until no further loss in weight occurs, at a low heat, not exceeding dull redness (approximately 550° C.). The ash should not fuse. Cool in a desiccator and weigh soon after reaching room temperature.

Fat (Ether Extract).—Dry 2–5 grams of the material as directed above under Moisture. If very fine, mix with an equal weight of clean, dry sand. Extract in a Soxhlet extractor with anhydrous ether for 16 hours. Dry the extract at 100° C. for 30 minutes, cool in a desiccator and weigh. Continue alternate drying and weighing at 30-minute intervals to constant weight. (Generally, 1–1.5 hours is sufficient.)

Crude Fiber.—Determine as directed on pages 527–529.

Acidity of Water Extract (Tentative).—Weigh 18 grams of the flour into a 500-cc. Erlenmeyer flask and add 200 cc. of CO_2-free water. Place the flask, loosely stoppered, for an hour in a water bath kept at 40° C., shaking occasionally. Filter through a dry, folded filter, returning the first 10–15 cc. of the filtrate to the filter. Titrate 100 cc. of the clear filtrate with 0.05 N NaOH and phenolphthalein. Each cc. of 0.05 N NaOH is equivalent to 0.05% acidity as lactic acid.

Sugars (Tentative).—Determine reducing sugars and sucrose as described under Total Sugars in Feed Stuffs (p. 617).

Protein.—Determine nitrogen by the Kjeldahl or Gunning or Kjeldahl-Gunning-Arnold method, as described on pages 87–89. Multiply the percentage of N by 5.7 to obtain the percentage of protein.

Alcohol-soluble Protein.—METHOD 1—BY NITROGEN DETERMINATION (TENTATIVE).—Transfer 4 grams of the flour to a 150–200-cc. bottle or Erlenmeyer flask and add 100 cc. of 70% alcohol (by volume), taking care that none of the material sticks to the bottom of the container. Shake thoroughly ten to twelve times at intervals of 30 minutes at room temperature, or shake continuously in a shaking machine for 1 hour, and then set aside overnight. Shake thoroughly once more, let settle and filter through a dry, folded filter, returning the first runnings to the filter until a clear filtrate is obtained. Pipette 50 cc. of the filtrate, equivalent to 2 grams of the sample, into a Kjeldahl flask, dilute with 100 cc. of water to prevent frothing during digestion and determine N as directed above under Protein.

METHOD 2.—BY POLARIZATION (TENTATIVE).—Weigh 15.97 grams of the flour into a 300-cc. flask and add 100 cc. of 65% alcohol by volume (sp. gr. 0.90). Shake at 30-minute intervals for 3 hours and let stand overnight. Filter through a dry, folded filter and polarize in a 200-mm. tube. Precipitate the proteins in 50 cc. of the filtrate by the addition of 5 cc. of Millon's reagent. Shake, filter, and polarize the filtrate in a 200-mm. tube. Multiply the reading in degrees Ventzke by 1.1 to correct for dilution and deduct the product from the first reading. This difference, multiplied by 0.2, gives the percentage of gliadin nitrogen.

Millon's Reagent.—Dissolve metallic Hg in an equal weight of conc. HNO_3 and dilute the solution with an equal volume of water. The freshly prepared solution must be used.

Protein Soluble in 5% K_2SO_4 Solution (Tentative).—Weigh 6 grams of the flour into a 200-cc. flask and introduce exactly 100 cc. of 5% K_2SO_4 solution. Shake at 30-minute intervals for 3 hours and let stand overnight or, preferably, agitate at moderate speed in a shaker for 1 hour, let settle 30 minutes, filter and determine the N in 50 cc. of the filtrate, as directed previously under Protein.

Globulin and Albumin* **and Amino Nitrogen (Tentative).**—Weigh 10 grams of the flour into a 500-cc. Erlenmeyer flask, add 250 cc. of 1% NaCl solution, stopper the flask and shake thoroughly. Let stand, with occasional shaking, for 3 hours, filter through a dry paper and evaporate 100 cc. of the filtrate to a small volume in a Kjeldahl flask with 5 cc. of conc. H_2SO_4. Add the remainder of the H_2SO_4, digest and determine the N. To a second 100 cc. of the filtrate add 5 cc. of 20% phosphotungstic acid solution, shake thoroughly, let settle and filter by decantation. Wash slightly with water, concentrate the filtrate with 5 cc. of H_2SO_4 in a Kjeldahl flask and determine the N (amino) as directed previously under Protein. Deduct the amino N from the N found in the first aliquot to obtain the N as globulin and albumin.

Glutenin (Tentative).—Deduct the sum of the N soluble in K_2SO_4 solution and the alcohol-soluble N from the total N, and multiply the difference by 5.7.

Cold Water Extract (Tentative).—Weigh 20 grams of the flour into a 500-cc. Erlenmeyer flask and add gradually 200 cc. of water at 10° C. or colder. Shake vigorously when about 50 cc. of water have been added and continue shaking during the addition of the remainder. Let stand at 10° C. for 40 minutes, shaking occasionally. Filter through a large, dry, coarse filter paper, returning the first runnings to the filter until a clear filtrate is obtained. Pipette 20 cc. of the clear filtrate into a tared dish, evaporate to dryness on the steam bath, and dry to constant weight in an oven at 100° C., weighing at periods of 30 minutes.

Gluten.—Bamihl Qualitative Test (Tentative).—Place a very small quantity (about 1.5 milligrams) of the flour on a microscope slide, add a drop of a water solution containing 0.02% of water-soluble eosin and mix by means of a cover-glass, holding the latter at first in such a manner that it is raised slightly above the slide, and taking care that none of the flour escapes from beneath it. Finally, let the cover-glass rest on the slide and rub it back and forth until the gluten has collected into rolls. The operation should be carried out on a white paper so that the formation of gluten rolls can be noted. Wheat flour, or other flours containing gluten, show by this treatment a copious amount

* Edestin and Leucosin.

of gluten, which absorbs the eosin with avidity, assuming a carmine color. Rye and corn flour yield only a trace of gluten, and buckwheat flour no appreciable amount. The preparations are best examined with the naked eye, thus gaining an idea of the amount of gluten present. If the flour is coarse, or contains a considerable amount of bran elements, as is true of buckwheat flour and low-grade wheat flour, the test should be made after bolting, as the bran particles and coarse lumps interfere with the formation of gluten rolls.

Quantitative Determination (Tentative).—Weigh 25 grams of the flour into a cup or porcelain mortar, add sufficient tap water (about 15 cc.) to form a firm dough-ball and work into a dough with a spatula or pestle, taking care that none of the material adheres to the utensil employed. Let the dough stand in water at room temperature for 1 hour, then knead gently in a stream of tap water until the starch and all soluble matters are removed. This operation requires approximately 12 minutes and should be performed over bolting cloth or a horse-hair sieve. To determine if the gluten is starch-free let 1 or 2 drops of the wash water, obtained by squeezing the gluten, fall into a beaker containing perfectly clear water. If starch is present, a cloudiness appears. Let the gluten thus obtained stand in water for 1 hour, then press as dry as posssible between the hands, roll into a ball, place in a tared, flat-bottomed dish and weigh as Moist Gluten. Transfer to an oven, dry to constant weight at 100° C. (about 24 hours), cool and weigh as Dry Gluten.

Chlorine.—Qualitative Test for Chlorine-bleached Flour (Tentative).—Extract 30 grams of the flour with gasoline and let the latter evaporate. A small amount of oil remains. Heat a piece of copper wire in a colorless gas flame until it is black and no longer colors the flame green. Dip the hot end of the wire into the oil and again into the flame. If chlorine or bromine has been used as a bleaching agent, a green or blue coloration is produced.

Quantitative Determination (Tentative).—Weigh 20 grams of the flour into a flat-bottomed aluminum dish, 8–10 cm. in diameter, and dry 5 hours at 100° C. Transfer, with as little exposure to the air as possible, to a continuous fat extractor, and extract for 16 hours with anhydrous, alcohol-free ether, which is also free from Cl. Transfer the ether extract to a platinum dish

and add 25 cc. of a solution containing 25 grams of NaOH and 15 grams of $NaNO_3$ per liter. Place the dish on the steam bath, evaporate to dryness and ignite in a muffle at a dull red heat until the contents are thoroughly charred. Extract the charred mass with 25 cc. of 1% HNO_3 and filter. Return the residue to the dish, char and again extract with 25 cc. of 1% HNO_3. Filter, wash with hot water, return to the dish and ignite to a white ash. Dissolve the ash in 5% HNO_3 and add the solution to the filtrates previously obtained. Determine the Cl in the combined filtrate either gravimetrically, weighing as AgCl, or volumetrically by the Volhardt Method, as described on page 763, using 0.02 N solutions for greater accuracy. Report results in parts of Cl per million.

NOTE.—In determining Cl special precautions should be taken that the air of the laboratory during the entire operation is not contaminated with Cl or HCl fumes and that all reagents used are as free as possible from Cl. In all cases conduct a blank determination at the same time and employ a correction if necessary.

Nitrite Nitrogen (Tentative).—REAGENTS.—(*a*) *Sulfanilic Acid Solution.*—Dissolve 0.5 gram of sulfanilic acid in 150 cc. of 20% acetic acid.

(*b*) *Alpha-naphthylamine Hydrochloride Solution.*—Dissolve, by heating, 0.2 gram of the salt in 150 cc. of 20% acetic acid.

(*c*) *Standard Nitrite Solution.*—Dissolve 0.1099 gram of dry $AgNO_2$ in about 20 cc. of hot water, add 0.10 gram of NaCl, shake until the AgCl flocculates and make up to 1 liter. Draw off 10 cc. of the clear solution and dilute to 1 liter. Each cc. of the last solution is equivalent to 0.0001 milligram of N as nitrite.

The $AgNO_2$ may be prepared as follows: To a cold solution of about 2 grams of $NaNO_2$ or KNO_2 in 50 cc. of water, add a solution of $AgNO_3$ as long as a precipitate appears. Decant the liquid and thoroughly wash the precipitate with cold water. Dissolve in boiling water. On cooling, the $AgNO_2$ crystallizes out. Dry the crystals in the dark at ordinary temperature (preferably in a vacuum).

DETERMINATION.—*Method 1.*—Select a series of 100-cc. volumetric flasks of uniform dimensions and color. Place 2 grams of high-grade, nitrite-free flour in each; add approximately 70 cc. of nitrite-free water and shake until the flour is thoroughly

moistened. Add to these flasks varying amounts of the standard nitrite solution, so that a series of comparison standards will be obtained having a range covering the probable nitrite content of the unknown sample. Reserve 1 flask for a blank test. In order to avoid making a large series of standards it is well to make a preliminary test to ascertain the approximate nitrite content of the unknown. Where the quantity of nitrite present is small, the nitrite solution in the flasks may be increased by 0.4 cc. each. Where bleaching is excessive, 1 gram of flour may be used throughout, or the standards may be given a wider variation in nitrite content.

To each of 2 similar flasks add 2 grams of the flour and 90 cc. of water; shake thoroughly and digest all the flasks, including the blank, in a water bath at 40° C. for at least 15 minutes. Add 2 cc. each of the sulfanilic acid and alphanaphthylamine hydrochloride solution to each flask, shaking the mixture after the addition of each reagent. Continue the digestion at 40° C. for an additional 20 minutes. The color must be developed in all the flasks under conditions as nearly uniform as possible. Dilute to the marks with nitrite-free water and compare the unknown with the series of standards. This may be done in a large, white-enameled pan, the effect of the turbidity, due to the flour, being minimized by the white background. The solutions should be allowed to subside and should not be shaken during comparison. Report results as parts of Nitrite Nitrogen per million.

Method 2.—Weigh 20 grams of the flour into a 500-cc. Erlenmeyer flask, add 200 cc. of nitrite-free water, previously warmed to 40° C., and close the flask with a rubber stopper. Shake vigorously for 5 minutes and digest for 1 hour in a water bath, keeping the temperature of the liquid in the flask at 40° C., and shaking at 10-minute intervals. Finally filter on a dry, nitrite-free, folded filter. Return the first runnings to the filter until a clear filtrate is obtained. Pipette 50 cc. of the filtrate and 50 cc. of the standard nitrite solution into small flasks; add to each 50 cc. of water and 2 cc. each of the sulfanilic acid and alphanaphthylamine hydrochloride solution; shake and let stand 1 hour to bring out the color. Compare the 2 solutions in a colorimeter. Divide the height of the column of the standard solution by that

of the solution of the sample to obtain the parts of N as nitrous acid (free and combined) per million of flour.

Gasoline Color Value (Tentative).—Place 20 grams of the flour in a wide-mouthed, glass-stoppered, 120-cc. bottle and add 100 cc. of *colorless* gasoline. Stopper tightly and shake vigorously for 5 minutes. After standing for 16 hours shake again for a few seconds until the flour has been loosened from the bottom of the bottle and thoroughly mixed with the gasoline, then filter immediately on a dry, 11-cm. paper into an Erlenmeyer flask, keeping the funnel covered with a watch glass to prevent evaporation. In order to secure a clear filtrate, let a certain quantity of the flour pass over upon the paper and pour the first portion of the filtrate through a second time. It will be found convenient to fit the filter paper to the funnel by means of water and dry thoroughly either by standing overnight in a well-ventilated place or by heating.

Determine the color value of the clear gasoline solution in a Schreiner or similar colorimeter, using for comparison a 0.005% K_2CrO_4 solution. This solution corresponds to a gasoline number of 1.0 and is conveniently prepared by diluting 10 cc. of a 0.5% solution to 1 liter. The colorimeter tube containing the gasoline solution should first be adjusted to read 50 mm., then the tube containing the standard chromate solution raised or lowered until the shades of yellow in both tubes match. The reading of the chromate solution, divided by the reading of the gasoline solution, gives the gasoline color value.

The color value may be determined also in Nessler tubes, using for comparison K_2CrO_4 solutions of various dilutions prepared from a 0.5% solution and filling the tubes in all cases to the height of 50 mm.

Alum (Qualitative Test).—Mix 10 grams of the sample with 10 cc. of water and stir in 1 cc. of logwood tincture (5 grams of logwood digested in 100 cc. of alcohol) and 1 cc. of a saturated solution of ammonium carbonate. If the sample is pure, the color will be faint pink or brown; but if alum is present, a distinct lavender-blue color is produced, which should remain after heating for 2 hours in a water oven.

Ergot.—Ergot is a fungous growth containing a poisonous alkaloid, sometimes developing in rye and less often in wheat.

Under the microscope it appears as a fine net-work of mostly colorless parenchyma cells, containing globules of fat.*

If flour containing ergot is treated with a very dilute solution of aniline violet, the stain will be practically absorbed by the damaged particles of the grain and resisted by the normal granules. A hot alcohol extract of flour containing ergot is colored red when treated with dil. H_2SO_4.

NOTE.—For baking tests and other tests on flour than given above, see Leach: "Food Inspection and Analysis," 4th ed.

MILK AND CREAM

MILK

General.—The sp. gr. of pure milk at 60° F. generally ranges from 1.027–1.035. Its average composition is approximately as follows:

		Per cent
Butter fat		3.6
Solids not fat:		
Casein	3.0	9.1
Other nitrogenous substances	0.8	
Lactose	4.5	
Citric acid	0.1	
Ash	0.7	
Total solids		12.7

According to the above figures, the composition of the *solids* should be as follows:

	Per cent
Casein	23.7
Lactose	35.5
Fat	28.4
Ash	5.5
Total protein	29.9

It will be seen that casein is about 80 per cent of the total protein.

The U. S. Federal Standard for pure milk (Bureau of Chemistry, *Circ.* 19) is as follows:

* See Leach: "Food Inspection and Analysis," 4th ed., 323.

	Per cent
Solids not fat	minimum 8.5
Milk fat	minimum 3.25

Skimmed milk should contain not less than 9.25% of milk solids.

The usual determinations in ascertaining the nutritive values of milk are Specific Gravity, Total Solids, Fat, Protein, Lactose, and Ash. The following methods, unless otherwise indicated, are the official methods of the Association of Official Agricultural Chemists.

Preparation of Sample.—Before withdrawing portions for analysis, bring the sample to 15–20° C. and mix well by pouring into a clean, dry receptacle and back until a homogeneous mixture is obtained. If lumps of cream do not completely disappear, warm to about 38° C., mix well, and then cool to 15–20° C. For determinations which require a measured volume, bring the milk to 20° C. before pipetting.

Specific Gravity.—Determine the sp. gr. at 15.5° C. with a pycnometer, first shaking the sample well.

Total Solids.—Heat 3–5 grams of the milk at the temperature of boiling water until it ceases to lose weight, using a tared, flat-bottomed dish of not less than 5-cm. diameter. If desired, previous to weighing the dish, place in it 15–20 grams of pure, dry sand. Cool in a desiccator and weigh rapidly to avoid absorption of hygroscopic moisture.

Ash.—Weigh quickly about 20 grams of the milk in a tared porcelain dish, add 6 cc. of conc. HNO_3, evaporate to dryness and ignite at a temperature just below redness until the ash is free from carbon. Cool in a desiccator and weigh the ash.

Acidity.—Weigh 10–20 cc. of the milk in a small flask, dilute with an equal volume of recently boiled and cooled water, add 0.5 cc. of phenolphthalein indicator and titrate with 0.1 N NaOH. Calculate the percentage of lactic acid.

Calculation.—1 cc. 0.1 N NaOH = 0.009 gram lactic acid.

Protein.—Place about 5 grams of the milk in a Kjeldahl digestion flask and determine the total N by the Kjeldahl or Gunning or the Kjeldahl-Gunning-Arnold method (pp. 87–89). Multiply the percentage of N by 6.38 to obtain the percentage of N compounds or Total Protein.

Casein.—This determination should be made while the milk is fresh or nearly so. If it cannot be made within 24 hours, add 1 part of formaldehyde to 2500 parts of the milk and keep in a cool place.

METHOD I.—Place 10 grams of the milk in a beaker with 90 cc. of water at 40–42° C. and add at once 1.5 cc. of dil. acetic acid (1:9). Stir and let stand 3–5 minutes. Then decant on a filter, wash by decantation two or three times with cold water and transfer the precipitate to the filter. Wash once or twice on the filter. The filtrate should be clear, or very nearly so. If the first portions of the filtrate are not clear, repeat the filtration, after which complete the washing of the precipitate. Determine N in the washed precipitate and filter paper as directed above, multiply by 6.38 and calculate the percentage of casein.

In samples of milk which have been preserved, the acetic acid should be added in small portions, a few drops at a time, with stirring, and the addition continued until the liquid above the precipitate becomes clear, or very nearly so.

METHOD II.—To 10 grams of the milk add 50 cc. of water at 40° C., then 2 cc. of a potash alum solution saturated at 40° C. or higher. Let the precipitate settle, transfer to a filter and wash with cold water. Determine N in the precipitate and filter paper as directed above, multiply by 6.38 and calculate the percentage of casein.

Albumin.—If Method I was used for determining the casein, exactly neutralize the filtrate from the acetic acid precipitation with 10% NaOH solution and add 0.3 cc. of dil. acetic acid (1:9). Heat on the steam bath until the albumin is completely precipitated. If Method II was used, add 0.3 cc. of the dil. acetic acid directly to the filtrate and boil to precipitate the albumin. Collect the precipitate on a filter, wash with cold water, and determine the N. Multiply the percentage of N, based on the original sample, by 6.38 to obtain the percentage of albumin.

Lactose.—Dilute 25 grams of the milk with 400 cc. of water in a 500-cc. volumetric flask. Add 10 cc. of Fehling's $CuSO_4$ solution (Soxhlet modification) and about 7.5 cc. of KOH solution of such strength that 1 volume is just sufficient to precipitate completely the Cu from 1 volume of the Fehling's solution. (Instead of KOH of this strength, 8.8 cc. of 0.5 N NaOH

solution may be used.) After the addition of the alkali solution, the mixture must still have an acid reaction and contain Cu in solution.

Dilute the solution to the mark, mix, filter through a dry filter and determine anhydrous lactose in an aliquot of the filtrate by the Munson and Walker method (p. 551).

Fat (Roese-Gottlieb Method).—Weigh 10–11 grams of the milk into a Röhrig tube or a similar apparatus, add 1.25 cc. of conc. NH_4OH (2 cc. if the sample is sour) and mix thoroughly. Add 10 cc. of 95% alcohol and mix well. Then add 25 cc. of ether, shake vigorously for 30 seconds, add 25 cc. of petroleum ether (redistilled slowly at a temperature below 60° C.) and shake again for 30 seconds. Let stand 20 minutes, or until the upper liquid is practically clear. Draw off as much as possible of the ether-fat solution (usually 0.5–0.8 cc. will be left) into a weighed flask through a small, rapid filter. (The flask should always be weighed with a similar one as a counter poise.) Re-extract the liquid remaining in the tube, this time with only 15 cc. of each ether, shake vigorously 30 seconds with each and let settle. Draw off the clear solution through the small filter into the same flask as before and wash the tip of the spigot, the funnel and the filter with a few cc. of a mixture of the 2 ethers in equal parts, free from suspended water. For absolutely exact results the re-extraction must be repeated. This third extraction yields not more than about 1 milligram of fat if the previous ether-fat solutions have been drawn off closely. Evaporate the ethers slowly on the steam bath, then dry the fat in a boiling water oven to constant weight.

Confirm the purity of the fat by dissolving in a little petroleum ether. Should a residue remain, remove the fat completely with petroleum ether, dry the residue, weigh and deduct the weight. Finally correct this weight by a blank determination on the reagents used.

Fat (Babcock Method).—Apparatus.*—(*a*) *Standard Babcock Test Bottles.*—The standard Babcock test bottles for milk and cream are as follows:

* The specifications for all apparatus for the Babcock test are given in detail in Association of Official Agricultural Chemists: "Methods of Analysis," 262–263, and 270–271 (1925).

(1) The 8%, 18-gram, 6-inch, Milk-test Bottle is shown in Fig. 37. It is 150–165 mm. tall, with the neck graduated from 0.0 to 8.0% in units, halves, and tenths of a per cent. The bulb may be cylindrical or conical and holds not less than 45 cc. up to the junction with the neck. The capacity of the neck for each whole per cent on the graduation is 0.20 cc. The charge for the bottle is 18 grams (17.6 cc.) of milk.

Fig. 37.—Babcock Milk-test Bottle.

(2) The 50%, 9-gram, Short-neck, 6-inch, Cream-test Bottle is 150–165 mm. tall, with the neck graduated from 0.0 to 50% for each 5%, 1% and 0.5%. The bulb is the same as that of the milk-test bottle. The capacity of the neck for each whole per cent on the graduation is 0.1 cc. The charge for the bottle is 9 grams of cream.

(3) The 50%, 9-gram, Long-neck, 9-inch, Cream-test Bottle is similar to the one described under (2) except that it is 210–229 mm. tall and the graduated portion of the neck is about twice as long.

(4) The 50%, 18-gram, Long-neck, 9-inch Cream-test Bottle is similar to the bottle described under (3) except that the charge is 18 grams of cream.

(*b*) *Centrifuge.*—The centrifuge must be capable, when filled to capacity, of rotating at the necessary speed with a minimum of vibration. The speed of revolution during the test is governed by the size as follows:

Diameter of wheel, inches	10	12	14	16	18	20	22	24
Revolutions per minute	1074	980	909	848	800	759	724	693

The diameter of the wheel is the distance between the inside bottoms of opposite cups measured through the center of rotation of the centrifuge wheel while the cups are horizontally extended. The centrifuge is heated to at least 55° C. during the test.

(*c*) *Pipette.*—The standard milk pipette is graduated to *contain* 17.6 cc. of water at 20° C. when the bottom of the meniscus coincides with the upper mark; delivery in 5–8 seconds. It should be tested by measuring from a burette the volume of water at 20° C. which it holds to the graduation mark and should be correct within 0.05 cc.

(*d*) *Acid Measure.*—This is graduated to *deliver* 17.5 cc. of conc. H_2SO_4 and may be a graduated cylinder or a pipette.

Calibration of Bottles.—Any suitable method may be used for the rapid testing of bottles, but the accuracy of any questionable bottle is to be determined by calibration with mercury. The bottle being first filled to zero with clean, dry Hg at 20° C., 13.5471 grams of the Hg is equal to 5% on the scale of an 18-gram bottle and 10% on a 9-gram bottle. The maximum error of the total graduation or any part of it should not exceed the volume of the smallest unit of the graduation.

Determination.—Transfer 18 grams of the prepared sample at 20° C., by means of the standard pipette, to the test bottle, blowing out the milk remaining in the tip of the pipette after free out-flow has ceased. Add 17.5 cc. of conc. H_2SO_4 (sp. gr. 1.82–1.83 at 20° C.), preferably not all at once, pouring it down the side of the neck so as to wash any traces of milk into the bulb. The H_2SO_4 should be at 15–20° C. Shake until all traces of curd have disappeared, then transfer the bottle to the centrifuge, counterbalance it, and whirl for 5 minutes after the proper speed has been obtained. Add soft water, not cooler than 60° C., until the bulb is filled, and whirl 2 minutes more. Add hot water until the liquid column approaches the top of the graduations and whirl 1 minute longer at 55–60° C. Transfer the bottle to a warm water bath kept at 55–60° C., immerse it to the level of the top of the fat column and leave it there until the column is in equilibrium and the lower fat surface has assumed final form. Remove from the bath, wipe the bottle and, by means of dividers or calipers, measure the fat column, in terms of percentage by weight, from its lower surface to the highest point of the upper meniscus.

Note.—The fat column at the time of measurement should be translucent, of a golden-yellow or amber color, and free from visible suspended particles. Reject any test in which the fat column is milky or shows the presence of curd or of charred matter, or in which the reading is indistinct or uncertain.

Gelatin (Qualitative Test).—To 10 cc. of the milk add an equal volume of acid $Hg(NO_3)_2$ solution (Hg dissolved in twice its weight of conc. HNO_3 and this solution diluted to 25 times its volume with water), shake the mixture, add 20 cc. of water,

shake again, let stand 5 minutes and filter. If much gelatin is present, the filtrate will be opalescent and cannot be obtained quite clear. To a portion of the filtrate contained in a test-tube, add an equal volume of saturated aqueous picric acid solution. A yellow precipitate will be produced in the presence of any considerable amount of gelatin, while smaller amounts will be indicated by a cloudiness. In the absence of gelatin the filtrate will remain perfectly clear.

Preservatives.—Proceed as directed on pages 531–538. To test for salicylic or benzoic acid, first acidify 100 cc. of the milk with 5 cc. of HCl (1 : 3), shake until curdled, filter and proceed with the clear filtrate.

To test for formaldehyde add to 10 cc. of the milk an equal volume of conc. HCl containing 2 cc. of 10% $FeCl_3$ solution to each liter of the acid. Heat to 80–90° C. directly over a free flame in a small casserole, rotating to break up the curd. A violet coloration indicates formaldehyde.

Coloring Matter (Leach Method).—Warm about 150 cc. of milk in a casserole over a flame and add about 5 cc. of dil. acetic acid (1 : 3), then slowly continue the heating nearly to the boiling point while stirring. Gather the curd, when possible, into one mass with a stirring rod and pour off the whey. If the curd breaks up into small flecks, separate from the whey by straining through a sieve or colander. Press the curd free from adhering liquid, transfer to a small flask and macerate for several hours, preferably overnight, with about 50 cc. of ether, the flask being tightly corked and shaken at intervals. Decant the ether extract into an evaporating dish, remove the ether by evaporation and test the fatty residue for annatto, as directed on page 521.

The curd of an uncolored milk is perfectly white after complete extraction with ether, as is also that of a milk colored with annatto. If the extracted fat-free curd is distinctly orange or yellowish in color, a coal-tar dye is indicated. In many cases, upon treating a lump of a fat-free curd in a test-tube with a little conc. HCl the color changes to pink, indicating the presence of a dye similar to aniline yellow or butter yellow or perhaps one of the acid azo yellows or oranges. In such cases, separate and identify the coloring matter present in the curd as directed on page 517. If aniline yellow, butter yellow, or other oil-soluble

dye is present, the greater part will be found in the ether extract containing the fat. In such cases, proceed as directed on page 520 under Oil-soluble Dyes.

In some cases the presence of coal-tar dyes can be detected by treating about 10 cc. of the milk directly with an equal volume of conc. HCl in a porcelain casserole, giving the dish a slight rotary motion. In the presence of some dyes the separated curd acquires a pink coloration.

Cream

General.—Cream samples should be analyzed as soon as possible and preferably not later than 3 days after collection. Immediately before drawing portions for the determinations mix the sample until it pours readily and a uniform emulsion has been obtained. If very thick, warm it to 30–35° C. and then mix. In case lumps of butter have separated, heat the sample to 40–50° C. by placing in warm water. Mix well and weigh out at once the portions for analysis. Take care not to overheat the sample, especially in the case of thin cream, thereby causing the fat to "oil off."

The Federal Standard* requires not less than 18.0% of butter fat and not more than 0.2% of acidity, calculated as lactic acid, in ordinary cream; and not less than 30% of butter fat in "whipping cream."

Total Solids.—Follow the same procedure as for Milk, using 2–3 grams of the sample.

Ash, Acidity, Protein, and Lactose.—Proceed as above under Milk.

Fat.—Follow the methods given above under Milk. For the extraction method weigh 5 grams of the homogeneous sample into a Röhrig tube or similar apparatus, dilute with water to about 10.5 cc. and proceed as directed.

For the Babcock method, weigh 9 or 18 grams, depending upon the fat content, into the corresponding standard Babcock cream bottle and add 8–12 cc. of the H_2SO_4, in the case of the 9-gram bottle, or 14–17 cc. in the case of the 18-gram bottle; or add acid until the mixture after shaking has assumed a chocolate-brown

* *U. S. Dept. of Agr., Circ.* 136.

color. Shake until all lumps have completely disappeared, then add 5–10 cc. of soft water at 60° C. or above. Transfer to the centrifuge, counterbalance, and whirl 5 minutes after attaining the proper speed. Add hot water until the liquid column approaches the top of the stem graduations, then whirl 1 minute longer at 55–60° C. Place in a water bath at 55°–60° C. and measure the fat column as described previously under Milk.

NOTE.—Glymol or clear white mineral oil of sp. gr. not greater than 0.85 at 20° C. (either with or without the addition of a little oil-soluble dye) may be used to aid in reading the fat column. A few drops only should be introduced into the bottle just before the reading is made. Do not drop it in but let it flow down the side of the neck. The surface separating the glymol and the fat is regarded as representing the upper limit of the fat column. (See also note at end of Babcock Method under Milk.)

Gelatin.—Follow the same procedure as for Milk.

Coloring Matter.—Follow the procedure on pages 517–521, particularly looking for oil-soluble dyes and annatto.

Preservatives.—Proceed as directed under Milk.

REFERENCE.—Association of Official Agricultural Chemists: "Methods of Analysis," 259 and 270 (1925).

CONDENSED MILK AND MILK POWDER

General.—Formerly, the common meaning of "condensed milk" in this country was milk which had been condensed and preserved with cane sugar. Milk which had been condensed without added sweetening was often termed "evaporated cream," although this term was a misnomer. Today, the terms condensed, evaporated, or concentrated milk are used to denote whole milk from which a considerable portion of the water has been evaporated. When the product contains added sugar it is designated as sweetened. When skimmed milk is evaporated, either plain or sweetened, it must be designated as such.

Dried milk or milk powder is the product obtained by removing practically all of the water from milk.

The Federal Standards* for these various products require the following minimum percentages:

* *U. S. Dept. Agr., Circ.* 136.

	Total solids	Milk solids	Milk fat
Evaporated milk	.....	25.5%	7.8%
Sweetened condensed milk	.....	28.0	8.0
Condensed skimmed milk	.....	20.0	.....
Sweetened condensed skimmed milk	.....	24.0	.....
Dried milk	95.0%	.....	26.0
Dried skimmed milk	95.0	.....	.....

Unsweetened Condensed Milk

Preparation of Sample.—Transfer the entire contents of a can to a large dish, stir well and pass through a fine strainer until a homogeneous mass is obtained. If a slight separation of fat occurs, warm the portion of the sample containing the separated fat to 30–35° C. and agitate until a uniform emulsion is obtained; then combine with the unheated portion and mix thoroughly. (If an appreciable quantity of fat has separated, so that a satisfactory emulsion cannot be formed, an accurate analysis is impossible.) On the sample thus prepared determine Fat, and Nitrogen and, if called for, test for Gelatin, Preservatives, and Coloring Matter. Dilute 40 grams of the homogeneous mass with 60 grams of water, mix thoroughly and use this mixture for all other determinations, correcting the results for dilution.

Total Solids and Ash.—Determine total solids on 4–5 grams of the diluted sample as described under Milk (p. 630). Ignite the residue at a low red heat until the ash is free from carbon, cool in a desiccator and weigh.

Fat.—Use the Roese-Gottlieb method as described under Milk (p. 632), weighing 4–5 grams of the undiluted sample into the extraction tube and diluting with water to about 10.5 cc. before extracting.

Total Nitrogen.—Determine N on 5 grams of the undiluted sample by the Gunning method (p. 88). Multiply the percentage of N by 6.38 to obtain the equivalent of nitrogenous compounds.

Casein and Albumin.—Using 10 grams of the diluted sample, follow the method under Milk (p. 631).

Lactose.—Follow the method described under Milk (p. 631), using the diluted sample.

Gelatin, Preservatives, and Coloring Matters.—Follow the procedures described under Milk (pp. 634–635).

Sweetened Condensed Milk

Preparation of Sample.—Warm the sample to 30–35° C., transfer to a dish sufficiently large to stir thoroughly, and make the whole mass homogeneous. Weigh 100 grams into a 500-cc. volumetric flask, dilute to the mark with water, and mix thoroughly. If the sample will not emulsify uniformly, weigh out each portion for analysis separately.

Total Solids and Moisture.—Pipette 10 cc. of the above solution into a small, weighed platinum dish, with a flat bottom, containing 15–20 grams of pure, dry sand or asbestos fiber, which has previously been ignited and weighed with the dish. Dry to constant weight at the temperature of boiling water, cool in a desiccator and weigh rapidly. Calculate the percentage of total solids.

Ash.—Pipette 10 cc. of the solution into a platinum dish, evaporate to dryness, and ignite at a heat not exceeding dull redness until free from carbon. If a carbon-free ash cannot be thus obtained, exhaust the charred mass with hot water, filter and wash the residue. Burn the filter and contents to ash in the dish, add the filtrate, evaporate to dryness, and ignite at dull redness until white or grayish white. Cool in a desiccator and weigh.

Protein.—Pipette 10 cc. of the prepared solution into a Kjeldahl flask and determine nitrogen by the Kjeldahl or Gunning or Kjeldahl-Gunning-Arnold method, as described on pages 87–89. Multiply the N by 6.38 to obtain the protein.

Lactose (Milk Sugar).—Dilute 100 cc. of the prepared solution in a 250-cc.volumetric flask to about 200 cc. Add 6 cc. of Fehling's copper sulfate solution (Soxhlet modification), dilute to the mark, and mix thoroughly. Filter through a dry filter and determine anhydrous lactose by the Defren-O'Sullivan method (p. 554).

Fat.—Weigh 4–5 grams of the original homogeneous sample into a Röhrig tube or similar apparatus, dilute with water to about 10.5 cc. and proceed as directed under Milk (p. 632).

NOTE.—The Adams method of extracting paper impregnated with the sample and dried does not always give reliable results on this class of materials.

Sucrose.—Calculate sucrose "by difference," deducting from 100% the sum of the percentages of moisture, ash, protein, lactose and fat.

Milk Solids.—These are the total solids, minus the sucrose.

DRIED MILK (POWDER)

Preparation of Sample.—Mix the whole sample very thoroughly and, if lumpy, break up the lumps and pass through a sieve.

Moisture.—Heat 1–2 grams in a platinum dish to constant weight at the temperature of boiling water. Cool in a desiccator and weigh. Report the loss as Moisture.

Ash.—Ignite the residue from the Moisture determination at dull redness and proceed as under Ash in Sweetened Condensed Milk above.

Protein.—Determine N in 2 grams of the sample by the Kjeldahl or Gunning or Kjeldahl-Gunning-Arnold method, as described on pages 87–89. Multiply the N by 6.38 to obtain the protein.

Lactose.—Weigh 10 grams, if the sample is unsweetened, and 20 grams if sweetened, into a 250-cc. volumetric flask. Add about 200 cc. of water and mix thoroughly. Add 6 cc. of Fehling's copper sulfate solution (Soxhlet modification) and dilute to the mark. Filter through a dry filter and determine lactose by the Munson and Walker procedure, as described on page 551.

Fat (Roese-Gottlieb Method).—Weigh accurately 0.5–0.75 gram of the sample into a Röhrig tube or similar apparatus, dilute with water to about 10.5 cc. and proceed as directed on page 632 for Milk. The flask in which the fat is finally collected should be weighed with a counterpoise consisting of another flask of approximately the same size and weight.

Sucrose and Milk Solids.—Calculate these as described above under Sweetened Condensed Milk.

REFERENCE.—Association of Official Agricultural Chemists: "Methods of Analysis," 272 (1925).

CHEESE

General.—The U. S. Government Standard for cheese according to *Circular* No. 136 is as follows: Cheese is the ripened product made from milk or cream by coagulating the casein with rennet or lactic acid, with or without the addition of ripening ferments and seasoning, and contains in the water-free substance not less than 50% of milk fat. It may also contain added coloring matter.

Cheese is sometimes adulterated by preserving with boric acid or borax (see p. 539 for detection).

The following procedures, unless otherwise indicated, are official methods of the Association of Official Agricultural Chemists.

Sampling.—When the cheese can be cut, take a narrow wedge-shaped segment reaching from the outer edge to the center. Cut into strips and pass 3 times through a sausage machine. When the cheese cannot be cut, take the sample with a cheese trier. If only 1 plug can be obtained, take it perpendicular to the surface of the cheese at a point $\frac{1}{3}$ the distance from the edge to the center, extending either entirely or half-way through. When possible, draw 3 plugs: 1 from the center, 1 from a point near the outer edge, and 1 from a point half-way between the other two. For inspection purposes reject the rind, but for investigations requiring the absolute amount of fat in the cheese include the rind in the sample. Either grind the plugs in a sausage machine or cut very finely and mix carefully, preferably the former.

Moisture (Tentative).—Place 10–15 grams of washed and ignited sea sand or 2–3 grams of acid-washed short-fiber asbestos (long fiber may be made suitable by rubbing through a fine sieve) in a flat-bottomed platinum dish, 6–7 cm. in diameter. Place in the dish a glass rod about 5 mm. in diameter and slightly longer than the diameter of the dish. Ignite, cool and weigh the dish and contents. Then weigh into the dish 4–5 grams of the sample, prepared as above, and mix the cheese and sand or asbestos intimately with the glass rod until the mass is homo-

geneous. Leave the mass in as loose a condition as possible to facilitate drying. Dry the mixture in an oven at 100° C. and weigh at intervals of 1–1.5 hours until the weight becomes constant. (Three weighings are usually sufficient.)

Ash.—Ignite the residue from the moisture determination cautiously to avoid spattering and remove the heat while the fat is burning off. When the flame has died out, complete the burning in a muffle at low redness. Cool in a desiccator and weigh the ash.

Salt.—Dissolve the ash from the above determination in dil. HNO_3 (1:9), and determine the chlorine, either gravimetrically as AgCl, or volumetrically by the Volhardt method, as on page 763. Calculate to NaCl.

CALCULATION.—$AgCl \times 0.4078 = NaCl.$

1 cc. 0.1 N $AgNO_3 = 0.005846$ gram NaCl.

Nitrogen.—Determine nitrogen by the Kjeldahl or Gunning or Kjeldahl-Gunning-Arnold method (pp. 87–89), using about 2 grams of the cheese, and multiply the percentage of N by 6.38 to obtain the percentage of nitrogen compounds.

Acidity.—To 10 grams of finely divided cheese add water at 40° C. until the volume equals 105 cc. Shake vigorously and filter. Titrate 25-cc. portions of the filtrate, representing 2.5 grams of the sample, with 0.1 N NaOH and phenolphthalein. Express results in terms of lactic acid.

CALCULATION.—1 cc. 0.1 N NaOH = 0.009 gram lactic acid.

Coloring Matters (Tentative).—Proceed according to page 517.

Fat.—PREPARATION OF SAMPLE.—(1) *Alkaline Extraction.*—Treat about 300 grams of cheese, cut into fragments the size of a pea, with 700 cc. of 5% KOH solution at 20° C. in a large, wide-necked flask. Shake vigorously to dissolve the casein. In 5–10 minutes the casein will be dissolved and the fat will rise to the surface in lumps. Collect into as large a mass as possible by shaking gently. Pour cold water into the flask until the fat is driven up into the neck and remove with a pipette. Wash the fat thus obtained with just sufficient water to remove any alkali. The fat is not perceptibly attacked by the alkali in this treatment and is practically all separated in a short time. It is then prepared for chemical analysis by filtering through a dry filter

paper in a hot water funnel at about 60° C. Refilter, if necessary, and dry.

(2) *Acid Extraction.*—Pass the cheese through a grinding machine; transfer to a large flask and cover with warm water, using 1 cc. for every gram of cheese. Shake thoroughly and add conc. H_2SO_4 slowly and in small quantities, shaking after each addition. The total amount of acid used should be the same as the amount of water. Remove the fat, which separates after standing a few minutes, by means of a separatory funnel, wash free from acid, filter and dry as above.

Examination of Fat.—Make such tests as are necessary on the fat by procedures described on pages 298, 310, and 319. As a general rule the sp. gr., refractive index, iodine number, and Reichert-Meissl number will be sufficient.

Quantitative Determination.—Cover the perforations on the bottom of an extraction tube with dry asbestos felt and place on this a mixture containing equal parts of anhydrous $CuSO_4$ and pure dry sand to a depth of about 5 cm., packing loosely. Cover the upper surface of this mixture with a layer of asbestos. Place on this 2–5 grams of the sample and extract with anhydrous ether for 5 hours in a continuous extraction apparatus. Remove the cheese and grind it with pure sand in a mortar to a fine powder. Return the mixed cheese and sand to the extraction tube, wash out the mortar with ether, add the washings to the tube and continue the extraction for at least 10 hours. Evaporate off the ether, dry the fat at 100° C., cool in a desiccator and weigh.

Reference.—Association of Official Agricultural Chemists: "Methods of Analysis" 278 (1925).

VINEGAR

General.—The term vinegar, when unqualified, is understood to mean cider vinegar (apple vinegar) made by fermentation of apple juice. Vinegar may also be made from other substances containing sugars or alcohol. Cider vinegar is laevorotatory; malt vinegar and glucose vinegar are dextrorotatory.

The Federal Standards* require a certain minimum content of various constituents in 100 cc. of the different kinds of vinegar (at 20° C.) as follows:

* *U. S. Dept. Agr., Circ.* 136.

Kind of vinegar	Cider (apple)	Wine (grape)	Malt	Sugar	Glucose	Spirit (distilled, grain)
Acetic acid, grams	4	4	4	4	4	4
Solids, grams	1.6*	1.0	2	....	....	....
Total ash, grams	0.25	0.13	0.2	....	....	....
Water-soluble P_2O_5, milligrams	10	....	9	....	....	....
Alkalinity of water-soluble ash, cc.	30	....	4	....	....	....

* Not more than 50% of this to be reducing sugars.

Preparation of Sample.—Before starting the analysis note the appearance, color, odor and taste. For microscopical examination employ the original sample, but for chemical analysis filter after thorough mixing, unless perfectly clear.

Calculation of Results.—Express all results in grams per 100 cc., unless otherwise noted.

Specific Gravity.—Determine the sp. gr. at 20°/4° C. by means of a pycnometer. The pycnometer should be warmed quickly to room temperature after filling and before weighing, to prevent the error due to collection of moisture on the outside. A small hole filed in the cap will permit the necessary expansion in the volume of the liquid.

Alcohol.—Measure 100 cc. of the sample into a round-bottomed distilling flask and make faintly alkaline with strong NaOH solution (1 : 1). Add a small scrap of paraffin, distill nearly 50 cc. and make up the distillate to 50 cc. at the temperature of the sample. Determine the sp. gr. very accurately with a pycnometer. Calculate the percentage by volume or grams of alcohol per 100 cc. from standard alcohol tables* bearing in mind that the alcoholic strength of the distillate is twice that of the original vinegar.

* Leach: "Food Inspection and Analysis," 4th ed., 690; Van Nostrand's "Chemical Annual;" Association of Official Agricultural Chemists: "Methods of Analysis," 464 (1925); *Bur. Standards, Circ.* 19. (The sp. gr. of the distillate must be determined at the temperature for which the alcohol table is calculated.)

Glycerol.—When it is necessary to determine the amount of glycerol, use the method described in Association of Official Agricultural Chemists: "Methods of Analysis," page 327 (1925).

Total Solids.—Measure 10 cc. of filtered vinegar into a weighed, flat-bottomed, platinum dish of 50-mm. bottom diameter. Evaporate on a boiling water bath for 30 minutes and dry for exactly 2.5 hours in the drying oven at the temperature of boiling water. Cool in a desiccator and weigh.

NOTE.—It is essential to use a flat-bottomed dish and follow directions exactly. We have found, however, that silica dishes may be used in place of platinum.

Total Reducing Substances before Inversion.—Pipette 25 cc. of the filtered sample into a 100-cc. volumetric flask and add sufficient strong NaOH solution (1 : 1) to nearly neutralize the acid. Cool, dilute to the mark with water, mix, and determine reducing sugars in 50 cc. of the solution by the Munson and Walker method (p. 551). In the case of malt vinegar express the result as dextrose; in all other cases, as invert sugar. (Malt vinegar should be clarified, if necessary, with sodium phosphotungstate.)

Total Reducing Substances after Inversion.—To 25 cc. of the sample in a 50-cc. volumetric flask add 2.5 cc. of conc. HCl, and carry out the inversion at 70° C., as described on page 549 under Invert Reading. Then neutralize with strong NaOH solution (1 : 1), make up to volume and determine reducing substances in 25 cc. of the solution by the Munson and Walker method.

Non-volatile Reducing Substances (Sugars).—Evaporate 50 cc. on the steam bath to a syrupy consistency, add 10 cc. of water and again evaporate. Add another 10 cc. of water and evaporate. Transfer to a 100-cc. volumetric flask with about 50 cc. of warm water. Cool, invert with 5 cc. of conc. HCl as previously described, nearly neutralize with NaOH solution, cool, dilute to the mark with water, and determine reducing sugars by the Munson and Walker method, using 20 or 40 cc. of the solution, depending upon the amount of sugars present. Calculate the result as invert sugar (as dextrose in the case of malt vinegar).

NOTE.—If the sample contains no sucrose, omit the inversion with HCl. Sucrose, if present, is calculated from the difference between the total reducing substances before and after inversion (see p. 550).

Polarization.—Decolorize 50 cc. of the sample with decolorizing carbon. Usually 0.5 gram is sufficient. Filter through a double filter and polarize at 20° C. in a 200-mm. tube. Report the polarization in degrees Ventzke.

Ash.—Measure 25 cc. into a weighed platinum dish. Evaporate to dryness on the steam bath and heat to a char at low heat, not exceeding dull redness. Treat the charred portion with a few cc. of water and filter through a quantitative filter. Ignite the filter paper and carbon in the platinum dish at low heat. Add the filtrate and evaporate to dryness. Ignite gently at dull redness, cool in a desiccator and weigh.

NOTE.—Useful information may often be obtained by noting the odor given off by the solids during charring.

Soluble and Insoluble Ash and Alkalinity.—Add to the above ash 10–15 cc. of water, bring nearly to a boil and filter through a 9-cm. quantitative filter. Wash with successive portions of hot water until the filtrate measures about 60–75 cc. Dry and ignite the filter with the undissolved residue at low red heat in the platinum dish. Cool, weigh and calculate as insoluble ash. Subtract from the total ash to obtain the soluble ash. Cool the filtrate and titrate with 0.1 N HCl and methyl orange. Express the alkalinity of the soluble ash as the number of cc. of 0.1 N HCl required per 100 cc. of sample.

Soluble and Insoluble Phosphoric Acid.—Determine the P_2O_5 in the water-soluble and water-insoluble portions of the ash by the official method for Fertilizers (p. 764), dissolving the water-insoluble portion in about 50 cc. of boiling HNO_3 (1 :8). Express results as milligrams of P_2O_5 per 100 cc. of vinegar.

Total Acids.—Dilute 10 cc. of the sample with recently boiled and cooled water until it appears very slightly colored and titrate with 0.5 N NaOH and phenolphthalein. Calculate results to acetic acid. For most purposes it is customary to report as Total Acidity, Calculated as Acetic Acid.

CALCULATION.—1 cc. 0.5 N NaOH = 0.0300 gram acetic acid.

NOTE.—Instead of using 0.5 N NaOH to titrate 10 cc., the 10 cc. may be diluted in a volumetric flask to 250 cc. and 50 cc. of this solution titrated with 0.1 N NaOH . (1 cc. 0.1 N NaOH = 0.00600 gram acetic acid).

Fixed Acids.—Measure 10 cc. into a 200-cc. porcelain casserole. Evaporate just to dryness, add 5–10 cc. of water, and again

evaporate. Repeat until at least 5 evaporations have taken place and no odor of acetic acid can be detected. Add about 200 cc. of recently boiled water and titrate with 0.1 N NaOH and phenolphthalein. Express the result as malic acid.

CALCULATION.—1 cc. 0.1 N NaOH = 0.0067 gram malic acid.

Volatile Acids.—Calculate the fixed acid as acetic and subtract from the total acid, also calculated as acetic. Report the difference as Volatile Acids, Calculated as Acetic Acid.

Esters.*—Dilute 200 cc. of the sample with 25 cc. of water and distill slowly into a 200-cc. volumetric flask until nearly filled to the mark. Complete the volume and mix well. Exactly neutralize 50 cc. of the distillate to phenolphthalein with 0.1 N NaOH, and add a measured excess of 25–50 cc. of the 0.1 N NaOH over the amount required for neutralization. Either boil for 1 hour with a reflux condenser, or let stand overnight in a stoppered flask, and then heat with a tube condenser for $\frac{1}{2}$ hour below the boiling point. Cool, and titrate the excess of NaOH with 0.1 N acid and phenolphthalein. Multiply the number of cc. of 0.1 N NaOH consumed in the saponification by 0.0088 to obtain the grams of esters, calculated as ethyl acetate. Multiply this by 2 to bring to the basis of 100 cc. Also report the Ester Number, which is the number of milligrams of KOH required to saponify the esters in 1 gram of the sample. For this purpose 1 gram of vinegar may be considered equivalent to 1 cc.

Formic Acid (Fincke Method).—Use the apparatus shown in Fig. 32 (p. 538). To 100 cc. of the sample in the flask *A* add 0.4–0.5 gram of tartaric acid and distill with steam. Pass the outflowing stream through a boiling mixture of 15 grams of $CaCO_3$ and 100 cc. of water in flask *B* and keep this volume as constant as possible throughout the process. Reduce the volume of the solution in the sample flask *A* to 30–40 cc. by heating with a small Tirrill flame. Collect 1000 cc. of distillate. Discard the distillate, disconnect the apparatus, filter the $CaCO_3$ mixture and wash with a little hot water. Make the filtrate slightly acid with HCl and add 10–15 cc. of mercuric chloride solution.† Heat on a boiling water bath for 2 hours, filter on a weighed Gooch

* This is not a method of the Association of Official Agricultural Chemists.

† To 10 grams of $HgCl_2$ and 15 grams of NaCl add sufficient water to make 100 cc.; mix well and filter.

crucible and wash the precipitate thoroughly with cold water and then with a little alcohol. Dry in a boiling water oven for 30 minutes, cool in a desiccator, and weigh as mercurous chloride. Calculate to formic acid.

CALCULATION.—$Hg_2Cl_2 \times 0.0975 =$ formic acid.

NOTES.—(1) The determinations usually required on a sample of vinegar, are sp. gr., total solids, and total acidity calculated as acetic acid.

(2) For other determinations than above described (alcohol precipitate, pentosans, tartaric acid, free mineral acid, dextrin, spices, coloring matters, preservatives, etc.) see Association of Official Agricultural Chemists: "Methods of Analysis," 330 (1925).

(3) The above methods, unless otherwise indicated, are essentially those of the Association of Official Agricultural Chemists.

ALMOND EXTRACT

Specific Gravity.—See page 653.

Alcohol.—As almond extract usually contains only about 1% of oil of almonds,* the alcohol may usually be calculated from the sp. gr. of the extract. If the extract is high in solids, determine the alcohol as follows:

Add 25 cc. of the extract, measured at 20° C., to 75 cc. of saturated NaCl solution in a separatory funnel and extract twice with 50-cc. portions of petroleum ether (b.p. 40–60° C.). Collect the petroleum ether extract in a second separatory funnel and wash twice with 2 separate 25-cc. portions of saturated brine. Combine the original salt solution with the washings; add a little powdered pumice, and distill into a 100-cc. volumetric flask. When almost 100 cc. have been distilled, make up with water to the mark at 20° C. and calculate the percentage of alcohol by volume from the sp. gr. at 20° C., as described on page 653.

Benzaldehyde.—Measure out 2 portions of 10 cc. each of the extract into 300-cc. Erlenmeyer flasks and add 10 cc. of phenylhydrazine reagent to one flask and 15 cc. to the other. Let stand in a dark place overnight. To each add 200 cc. of water and filter on a tared Gooch crucible provided with a thin mat of asbestos. Wash first with cold water and then with 10 cc. of 10% alcohol and dry at 70° C. for 3 hours at a pressure of not over 100 mm. of mercury or to constant weight over conc. H_2SO_4.

* The Federal Standard (*U. S. Dept. Agr., Circ.* 136) requires not less than 1%.

The weight of the precipitate multiplied by the factor 5.41 will give the weight of benzaldehyde in 100 cc. of the sample.

NOTE.—If the duplicate determinations do not agree, repeat using a larger quantity of the reagent.

Phenylhydrazine Reagent.—Add 3 cc. of glacial acetic acid to 40 cc. of water and mix with 2 cc. of phenylhydrazine.

Benzoic Acid.—Measure 10 cc. of the extract into a 100-cc. flask, add 10 cc. of 10% NaOH solution and 20 cc. of 3% H_2O_2 solution; cover with a watch glass and place in a water oven. Oxidation of the aldehyde to benzoic acid begins almost immediately and should be continued 5–10 minutes after all odor of benzaldehyde has disappeared, which usually requires 20–30 minutes. Remove the flask from the water oven and transfer the contents to a separatory funnel, rinsing off the watch glass. Add 10 cc. of dil. H_2SO_4 (1:5) and cool the contents of the funnel to room temperature under the water tap. Extract the benzoic acid with 4 portions of 25, 25, 20 and 20 cc. of ether, respectively, and wash the combined extracts with 2 portions of 5–10 cc. of water, or until all H_2SO_4 is removed. Filter into a tared dish, evaporate at room temperature, dry overnight in a desiccator and weigh the benzoic acid. Multiply the result in grams by 10.

Multiply the grams of benzaldehyde per 100 cc., obtained previously, by 1.151 to obtain the equivalent of benzoic acid, and subtract this from the grams of total benzoic acid per 100 cc. obtained above. The difference is the grams of benzoic acid per 100 cc. of the extract.

Hydrocyanic Acid.—*Qualitative Test.*—Add several drops of freshly prepared 3% $FeSO_4$ solution and a single drop of 1% $FeCl_3$ solution to several cc. of the extract. Mix thoroughly and add 10% NaOH solution drop by drop until no further precipitate forms and finally sufficient dil. H_2SO_4 (1:9) to dissolve the precipitate. In the presence of even small amounts of HCN, a Prussian-blue coloration or suspension will develop.

Quantitative Determination (In the Absence of Chlorides).—Measure into a small flask 25 cc. of the extract and add 5 cc. of freshly precipitated $Mg(OH)_2$, free from Cl. Titrate with 0.1 N $AgNO_3$, using K_2CrO_4 as indicator. Calculate to HCN.

CALCULATION.—1 cc. 0.1 N $AgNO_3 = 0.00270$ gram HCN.

Nitrobenzol (Qualitative Test).—Boil a few cc. of the extract with Zn dust and acetic acid and filter. Add to the filtrate a drop of $CHCl_3$, make strongly alkaline with 10% NaOH solution and heat. If nitrobenzol is present in the extract, the characteristic odor of phenylisonitrile will develop.

Reference.—The above are the tentative methods of the Association of Official Agricultural Chemists as published in its "Methods of Analysis," 356 (1925).

CASSIA, CINNAMON, AND CLOVE EXTRACTS

Oil (Hortvet and West Method).—Transfer 10 cc. of the extract to a separatory funnel, add 30 cc. of water, acidify with 1 cc. of dil. HCl (1:1) and extract three times with ether, using not less than 100 cc. altogether. Wash the combined ether solutions twice with water and, in the case of cinnamon extract, dry by shaking with a small amount of *granulated* $CaCl_2$. Transfer to a wide-mouthed, tared weighing bottle and evaporate the ether as rapidly as possible on a boiling water bath, rotating the liquid upon the sides of the flask in order to get rid of traces of ether. Weigh the residue and divide the weight by the sp. gr. of the oil in order to obtain the percentage of oil by volume. In the case of clove oil, let the weighing bottle remain in the balance case until the usual film of moisture has evaporated. The time of weighing, however, should not be delayed over 3 minutes.

Determine the refractive index of the residual oils at 20° C.

Dissolve a drop of the oil in several drops of alcohol, and add a drop of 10% $FeCl_3$ solution.

The following table gives the sp. gr., refractive index and color reaction with $FeCl_3$ for the 3 oils:

Table XXV—Characteristics of Cassia, Cinnamon, and Clove Oils

Oil	Sp. gr.	Refractive index at 20° C.	Color with $FeCl_3$ solution
Cassia	1.05	1.585–1.600	Brown
Cinnamon	1.03	1.590–1.599	Green
Clove	1.055	1.560–1.565	Deep blue

Alcohol.—With most extracts, which contain only about 2% of oil, the alcohol may be calculated from the sp. gr. of the original material. If the extract is high in solids, however, proceed as described under Almond Extract on page 648.

In calculating the alcohol from the sp. gr. of the extract, let

S = sp. gr. of extract,
O = sp. gr. of the oil,
and p = percentage of oil found.

Then $100-p$ will be the percentage of the water-alcohol solution, the sp. gr. of which, represented by W, is calculated as follows:

$$S=\frac{Op+W(100-p)}{100}, \text{ whence } W=\frac{100S-Op}{100-p}.$$

The percentage of alcohol A in the water-alcohol solution is obtained from standard alcohol tables. The percentage by volume of alcohol in the extract $=A\left(\frac{100-p}{100}\right)$.

The value for O, the sp. gr. of the oil, is given in the above table.

Note.—The Federal Standard requires that these extracts shall contain not less than 2% of the essential oil.

Reference.—Association of Official Agricultural Chemists, "Methods of Analysis," 205 (1925); *J. Assoc. Off. Agr. Chem.*, **5**, 308 (1922).

GINGER EXTRACT

Alcohol.—(*a*) *By Weight.*—Pipette 25 cc. of the sample at 15.5° C. (see note) into a small weighed flask and weigh it. Transfer to a distilling flask with 100 cc. of water. Distill nearly 100 cc. through a vertical condenser and either weigh the distillate or make to volume at 15.5° C. In either case determine the sp. gr. at this temperature. Obtain the percentage of alcohol by weight corresponding to the sp. gr. from standard alcohol tables;* multiply this figure by the weight of the distillate and divide by the weight of the sample taken to obtain the percentage by weight of alcohol.

* These may be found in Van Nostrand's "Chemical Annual," and in Leach's "Food Inspection and Analysis," 661 (1914).

(*b*) *By Volume.*—From the sp. gr. of the distillate obtained as above find the percentage of alcohol by volume from the alcohol tables; multiply this figure by the volume of the distillate and divide by the volume of the sample to obtain the percentage of alcohol by volume in the original material.

NOTE.—If the alcohol tables are calculated at 20° C. make all determinations at 20° C. instead of 15.5° C.

Solids.—Evaporate 10 cc. of the extract nearly to dryness on the steam bath, dry for 2 hours in an oven at 100° C. and weigh.

Test for Ginger (Seeker Method).—Dilute 10 cc. of the extract to 30 cc., evaporate to 20 cc., decant into a separatory funnel and extract with an equal volume of ether. Evaporate the ether spontaneously in a porcelain dish and to the residue add 5 cc. of 75% H_2SO_4 and about 5 milligrams of vanillin. Let stand 15 minutes and add an equal volume of water. In the presence of ginger extract an azure-blue color develops.*

Capsicum (Modified LaWall Test).—To 10 cc. of the extract add cautiously dil. NaOH solution until the mixture reacts very slightly alkaline to litmus paper. Evaporate at about 70° C. to approximately $\frac{1}{4}$ the original volume and render slightly acid to litmus paper with dil. H_2SO_4. Transfer to a separatory funnel, rinsing the dish with water, and extract with an equal volume of ether, avoiding emulsification by shaking the funnel gently 1–2 minutes. Draw off the lower layer and wash the ether extract once with about 10 cc. of water. Transfer the washed ether extract to a small evaporating dish, make decidedly alkaline with 0.5 N alcoholic KOH and evaporate at about 70° C. until the residue is pasty; then add about 20 cc. more of 0.5 N alcoholic KOH and let stand on the steam bath until the gingerol is completely saponified (about 30 minutes). Dissolve the residue in a little water and transfer with water to a small separatory funnel. The volume should not exceed 50 cc. Extract the alkaline solution with an equal volume of ether. Wash the ether extract repeatedly with small amounts of water until no longer alkaline to litmus. Transfer the washed extract to a small evaporating dish, and let the ether evaporate spontaneously. Finally test the residue for capsicum by moistening the tip of the

* We have found that this color sometimes does not develop unless the solution is warmed.

finger, rubbing it on the bottom and sides of the dish, and then applying the finger to the end of the tongue. A hot, stinging, or prickly sensation, which persists for several minutes, indicates capsicum or other foreign pungent substances.

REFERENCE.—These are essentially the tentative methods of the Association of Official Agricultural Chemists, published in its "Methods of Analysis," 358 (1925).

LEMON AND ORANGE EXTRACTS

Specific Gravity.—Determine the sp. gr. at 15.5° C. with a pycnometer, compared with water at the same temperature.

Alcohol.—Dilute 50 cc. of the extract, measured at 15.5° C., in a 200-cc. volumetric flask nearly to the mark. Let stand until the oil separates in a clear layer on top (or if necessary, centrifugalize). Then make up to the mark at 15.5° C., using the lower meniscus of the oil. Pour the mixture into a dry Erlenmeyer flask containing 5 grams of light $MgCO_3$, stopper, shake well and filter quickly through a large dry folded filter. Determine the alcohol in the filtrate as follows:

(*a*) BY WEIGHT.—Place 150 cc. of the filtrate, measured at 15.5° C., in a 300–500-cc. distilling flask. Attach the flask to a vertical condenser and distill, catching the distillate in a 100-cc. volumetric flask. Stop the distillation when nearly 100 cc. have been distilled. Make up to the mark with water at 15.5° C. and mix thoroughly. Determine the sp. gr. accurately with a pycnometer. Ascertain from standard alcohol tables the percentage of alcohol by weight corresponding to the sp. gr. of the distillate. Multiply this figure by the weight of the distillate (its volume × sp. gr.) and divide by the weight of the sample in the aliquot taken, *i.e.*, 37.5 × its sp. gr.

(*b*) BY VOLUME.—From the sp. gr. of the distillate, obtained as above, ascertain the percentage of alcohol by volume from the alcohol tables. Multiply this figure by the volume of distillate and divide by the volume of the original sample, *i.e.*, 37.5.

NOTES.—(1) References to standard alcohol tables are given on page 644.

(2) In case alcohol tables are used which are based on a gravity at some other temperature than 15.5° C., the sp. gr. of the original sample and of the alcohol distillate must be determined at the same temperature as that on which the tables are based.

(3) If the extract contains nothing besides oil, alcohol, and water, the alcohol may be calculated from the sp. gr. of the extract as described under Cassia Extract on page 651. For the sp. gr. of the oil (*O* in the formula) use 0.86 for lemon and 0.85 for orange.

Glycerol.—Evaporate 100 cc. of the extract* in a porcelain dish on a water bath to a volume of about 10 cc., treat the residue with about 5 grams of fine sand and 4–5 cc. of milk of lime (containing about 15% of CaO) for each gram of extract present, and evaporate almost to dryness. Treat the moist residue with 50 cc. of 90% alcohol by volume, remove the substance adhering to the sides of the dish with a spatula, and rub the whole mass to a paste. Heat the mixture on the water bath, with constant stirring, to incipient boiling and decant the liquid through a filter into a small flask. Wash the residue repeatedly by decantation with 10-cc. portions of hot 90% alcohol until the filtrate amounts to about 150 cc. Evaporate the filtrate to a syrupy consistency in a porcelain dish, on a hot, but not boiling, water bath; transfer the residue to a small glass-stoppered graduated cylinder with 20 cc. of absolute alcohol and add 3 portions of 10 cc. each of absolute ether, thoroughly shaking after each addition. Let stand until clear, then pour off through a filter and wash the cylinder and filter with a mixture of 2 parts of absolute alcohol and 3 parts of anhydrous ether, pouring the wash liquor also through the filter. Evaporate the filtrate to a syrupy consistency, dry for 1 hour at the temperature of boiling water, weigh, ignite, and weigh again. The loss on ignition gives the weight of glycerol.

Lemon and Orange Oils.—(*a*) By Polarization.—Polarize the extract at 20° C. without dilution in a 200-mm. tube and divide the reading in degrees Ventzke by 3.2, in the case of lemon extract, and by 5.2, in the case of orange extract. In the absence of other optically active substances, the result will be the percentage of oil by volume. A small amount of cane sugar is occasionally present; if so, determine it as directed under Sucrose and correct the reading accordingly.

(*b*) By Precipitation.—Pipette 20 cc. of the extract into a Babcock milk bottle; add 1 cc. of dil. HCl (1 : 1); then add 25–28 cc. of water previously warmed to 60° C.; mix and let

* If 100 cc. contain more than 0.4 gram of glycerol, use a smaller amount.

stand in water at 60° C. for 5 minutes; whirl in a centrifuge for 5 minutes; fill with warm water to bring the oil into the graduated neck of the bottle; repeat the whirling for 2 minutes; stand the flask in water at 60° C. for a few minutes and read the percentage of oil by volume. In case oil is present in amounts over 2%, add to the percentage of oil found 0.4%, to correct for the oil retained in solution. If less than 2% and more than 1% is present, add 0.3% for correction.

To obtain the percentage by weight from the percentage by volume, as found by either of the above methods, multiply the volume percentage by 0.86* and divide the result by the sp. gr. of the original extract.

NOTE.—The Federal Standard (*U. S. Dept. Agr., Circ.* 136) requires not less than 5% of lemon or orange oil in lemon and orange extracts.

Total Aldehydes (Chace Method).—REAGENTS.—(1) *Aldehyde-free Alcohol.*—Allow alcohol (95% by volume), containing 5 grams of meta-phenylenediamine hydrochloride per liter, to stand for at least 24 hours with frequent shaking. Boil under a reflux condenser for at least 8 hours (longer if necessary), let stand overnight and distill, rejecting the first 10% and the last 5% which come over. Keep in a dark, cool place in well-filled bottles. 25 cc. of this alcohol, on standing for 20 minutes in a cooling bath at 14–16° C. with 20 cc. of sulfite-fuchsin solution, should develop only a faint pink coloration. If a stronger color is developed, treat it again with meta-phenylenediamine hydrochloride.

(2) *Sulfite-fuchsin Solution.*—Dissolve 0.5 gram of fuchsin in 250 cc. of water, add an aqueous solution of SO_2 containing 16 grams of the gas and let stand until colorless or nearly so. Then make up to 1 liter with water. Let the solution stand 12 hours before using. It should be kept in a refrigerator and discarded after 3 days.

(3) *Standard Citral Solution.*—Weigh 0.5 gram of citral into a 50-cc. volumetric flask, dilute to the mark with the aldehyde-free alcohol at room temperature and mix well. Dilute 10 cc. of this solution to 100 cc. with aldehyde-free alcohol and mix well. The last solution contains 1 milligram of citral per cc.

*This is for lemon oil; use 0.85 for orange.

DETERMINATION.—Weigh in a stoppered weighing bottle approximately 25 grams of the extract, transfer to a 50-cc. volumetric flask, and make up to the mark at room temperature with aldehyde-free alcohol. Measure at room temperature 2 cc. of this solution into a comparison tube. Add 25 cc. of the aldehyde-free alcohol (previously cooled to 14–16° C.), then 20 cc. of the sulfite-fuchsin solution (also cooled) and finally make up to the 50-cc. mark with more aldehyde-free alcohol. Mix thoroughly, stopper, and keep at 14–16° C. for 15 minutes. Prepare a standard for comparison at the same time and in the same manner, using 2 cc. of the standard citral solution, and compare the colors developed. Calculate the amount of citral present. Repeat the determination, using a quantity sufficient to give the sample approximately the strength of the standard. From this result calculate the amount of citral in the sample. If the comparisons are made with Nessler tubes, standards containing 1, 1.5, 2, 2.5, 3, 3.5, and 4 milligrams, respectively, of citral should be prepared and the trial comparisons made against these, the final comparison being made with standards between 1.5 and 2.5 milligrams with 0.25 milligram increments.

NOTE.—It is absolutely essential to keep the reagents and the comparison tubes at the required temperature. Comparisons should be made within 1 minute after removing the tubes from the bath. Give the samples and standards identical treatment.

Citral (Hiltner Method).—REAGENTS.—(1) *Meta-phenylenediamine Hydrochloride Solution.*—Prepare a 1% solution of meta-phenylenediamine hydrochloride in 95% alcohol. Decolorize if necessary by shaking with fuller's earth and filter through a double filter. The solution should be bright and clear, free from suspended matter, and practically colorless. It is well to prepare only enough solution for the day's work, as it darkens on standing.

(2) *Alcohol.*—For the analysis of lemon extracts, 90–95% alcohol (by volume) should be used; but for terpeneless extracts, alcohol of 40–50% strength is sufficient. Filter to remove any suspended matter. The alcohol need not be purified from aldehyde. If not practically colorless, render slightly alkaline with NaOH and distill.

Determination.—All of the operations may be carried on at room temperature. Weigh 25 grams of the extract into a 50-cc. volumetric flask and make up to the mark with alcohol. Stopper the flask and mix the contents thoroughly. Pipette 2 cc. of this solution into a Nessler tube, add 10 cc. of meta-phenylenediamine hydrochloride reagent and complete the volume to 50 cc. with alcohol. Compare at once the color with that of the standard prepared at the same time, using 2 cc. of standard citral solution and 10 cc. of the meta-phenylenediamine reagent, and diluting to volume with alcohol. From the result of this first determination calculate the amount of standard citral solution that should be used in order to give approximately the same citral strength of the sample under examination,then repeat the comparison against the new standard.

Total Solids.—Evaporate nearly to dryness 10 cc. of the sample in a flat platinum dish on a water bath at a low temperature. Heat the residue for 2.5 hours in a drying oven at 100° C., cool and weigh.

Ash.—Burn the residue of total solids to a white ash at the lowest possible heat (not exceeding dull redness), cool and weigh.

Sucrose.—Neutralize the normal weight of the extract, evaporate to dryness, wash several times with ether, dissolve in water and determine sucrose in the usual manner by means of a polariscope (p. 548), or by copper reduction (p. 550).

Methyl Alcohol (Riche and Bardy Method).—Test the distillate obtained in the determination of Alcohol above for methyl alcohol as follows: Place 10 cc. in a small flask with 15 grams of iodine and 2 grams of red phosphorus. Keep in ice water for 10–15 minutes or until action has ceased. Distill off on the water bath the methyl and ethyl iodides formed into about 30 cc. of water. Wash with dil. NaOH solution to eliminate free iodine, separate the heavy oily liquid which settles and transfer to a flask containing 5 cc. of aniline. If the action is too violent, place the flask in cold water; if too slow, warm the flask gently. After 1 hour, boil the product with water and add about 20 cc. of 15% NaOH solution. When the bases rise to the top as an oily layer, fill the flask up to the neck with water and draw them off with a pipette. Oxidize 1 cc. of the oily liquid by adding 10 grams of a mixture of 100 parts of clean sand, 2 of common salt and 3 of

$Cu(NO_3)_2$. Mix thoroughly, transfer to a glass tube and heat to 90° C. for 8–10 hours. Exhaust the product with warm alcohol, filter and make up to 100 cc. with alcohol. If the sample is free from methyl alcohol, the liquid has a red tint, but in the presence of 1% of methyl alcohol it has a distinct violet shade; with 2.5% the shade is very distinct, and still more so with 5%. To detect more minute quantities of methyl alcohol, dilute 5 cc. of the colored liquid to 100 cc. with water, and dilute 5 cc. of this again to 400 cc. Heat the liquid thus obtained in a porcelain dish and immerse in it a fragment of white merino yarn (free from sulfur) for 30 minutes. If the ethyl alcohol is pure, the wool will remain white, but if methyl alcohol is present, it will become violet, and the depth of the tint will give a fairly approximate indication of the proportion of methyl alcohol present.

NOTE.—The presence of methyl alcohol and its approximate amount may also be ascertained by determining the refraction at 20° C. with the immersion refractometer. [See Association of Official Agricultural Chemists: "Methods of Analysis," 372 (1925).]

Coloring Matter.—(*a*) LEMON AND ORANGE PEEL COLOR.—Place a few cc. of the extract in a test-tube and add slowly 3-4 volumes of conc. HCl. Place a few cc. of the extract in a second tube and add several drops of conc. NH_4OH. If the color is due to the presence of lemon or orange peel only, it is materially deepened in both cases.

(*b*) TURMERIC.—Evaporate 25–50 cc. of the extract upon a small piece of filter paper, dry at low temperature, and moisten with a weak solution of boric acid containing a small amount of HCl. Upon drying a second time a cherry-red color, changing to green when spotted with NH_4OH, develops in the presence of turmeric.

REFERENCE.—Association of Official Agricultural Chemists: "Methods of Analysis" (1925).

LEMON AND ORANGE OILS

General.—According to the Federal Standards,* Orange Oil is the volatile oil obtained from the fresh peel of the orange and

* *U. S. Dept. Agr., Circ.* 136.

has an optical rotation at 25°C. of not less than +95° in a 100-mm. tube. Lemon Oil is obtained from the fresh peel of the lemon and has an optical rotation at 25° C. of not less than +60° in a 100-mm. tube and contains not less than 4% by weight of citral.

Specific Gravity.—Determine the sp. gr. at 20° C. with a Westphal balance.

Refractive Index.—Determine the refractive index at 20° C. with the Abbé refractometer.

Optical Rotation.—Determine the rotation at 25° C. with any standard instrument, using a 50-mm. tube and sodium light. The results should be stated in angular degrees on a 100-mm. basis. If instruments having the sugar scale are used, the reading on orange oil is above the range of the scale, but readings may be obtained by the use of standard laevorotatory quartz plates or by the use of a 25-mm. tube. The true rotation cannot be obtained by diluting the oil with alcohol and correcting proportionately.

Citral (Hiltner Method).—Proceed as directed under Lemon and Orange Extracts (p. 656), weighing 2 grams of lemon oil or 8 grams of orange oil into a 100-cc. volumetric flask, diluting to 100 cc. with 95% alcohol by volume and using 2 cc. of this solution for the comparison.

Total Aldehydes.—Weigh a small quantity of the sample into a small stoppered flask and dilute with aldehyde-free alcohol in the proportion of 2 grams of lemon oil or 4 grams of orange oil to 100 cc. of solution. Determine the total aldehydes as described on page 655 for Orange and Lemon Extracts (Chace Method), expressing the result as citral.

Reference.—Association of Official Agricultural Chemists: "Methods of Analysis," 355 (1925).

OIL OF PEPPERMINT

General.—Oil of Peppermint is the volatile oil obtained from peppermint. The Federal Standard* requires that it contain not less than 50% of menthol by weight.

Specific Gravity.—Determine the sp. gr. at 20° C. with a Westphal balance.

* *U. S. Dept. Agr., Circ.* 136.

Refractive Index.—Determine the refractive index with the Abbé refractometer at 25° C.

Specific Rotation, $[\alpha]_D^{20}$.—Determine the angle of refraction by means of the polariscope. Have the temperature exactly 20° C. and use a sodium light.* Calculate the specific rotation, $[\alpha]_D^{20}$, from the following formula:

$$[\alpha]_D^{20} = \frac{a}{L} \times \frac{100}{\text{sp. gr. at } 20° \text{ C.}};$$

where a = angle of refraction,
and L = length of tube in mm.

Dimethyl Sulfide.—Distill 1 cc. from 25 cc. of oil and pour the distillate on an aqueous solution of $HgCl_2$. A white film forming after a short time at the zone of contact indicates dimethyl sulfide, which is found in non-rectified oils.

Menthyl Esters.—Saponify 8–10 grams of oil by boiling for 1 hour with 25 cc. of 0.5 N alcoholic KOH in a flask provided with a reflux condenser. After cooling, titrate with 0.5 N HCl and phenolphthalein.

Multiply the number of cc. of KOH solution consumed in the saponification by 9.9 and divide the product by the weight of oil taken. This gives the percentage of esters as menthyl acetate.

Total Menthol.—Wash the residual oil from the ester determination with water a number of times, transfer to an acetylization flask (preferably a flask with a ground-glass tube condenser), add 10 cc. of acetic anhydride and 1 gram of anhydrous sodium acetate, and boil gently for 1 hour. Cool, wash the acetylized oil with water, and then with very dilute NaOH solution, until the mixture is slightly alkaline to phenolphthalein. Separate the oil from any water in a separatory funnel, pour into a small flask, add a few pieces of fused $CaCl_2$, let stand for several hours, and filter.

Weigh out 3–6 grams of this dry acetylized oil in an Erlenmeyer flask and saponify by boiling for 1 hour with 50 cc. of 0.5 N alcoholic KOH. After cooling, titrate the excess alkali with 0.5 N HCl.

Each cc. of 0.5 N alcoholic KOH consumed corresponds to 0.0781 gram of menthol, or 0.0991 gram of menthyl acetate. In

* In case the reading is taken with the Ventzke saccharimeter, using gas or other white light, calculate the saccharimeter reading to angular reading by multiplying the former by 0.3468.

order, therefore, to obtain the percentage of menthol in the original oil (not acetylized but freed from ester), it is necessary to deduct from the weight of the acetylized oil taken 0 0210 gram (the difference between 0.0781 and 0.0991) for every cc of 0.5 N alkali consumed. The following formula, therefore, gives the total menthol content (free and ester):

$$P = \frac{7.81a}{S - 0.0210a},$$

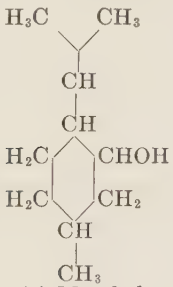
where P = percentage of total menthol;
S = grams of acetylized oil taken;
and a = cc. of 0.5 N alkali consumed.

By subtracting the menthol equivalent of the amount of ester as first determined, the amount of free menthol is obtained.

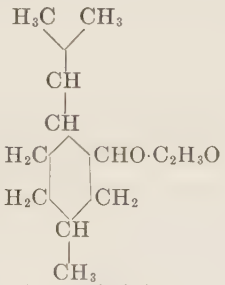
CALCULATION.—Menthyl acetate $\times 0.788$ = menthol.

NOTE.—The chemistry of the foregoing method is as follows:

Menthol is a saturated secondary alcohol of the structural formula (*a*) shown below. The ester has the formula (*b*).



(*a*) Menthol



(*b*) Menthyl Acetate

In the ester determination the acetate radical is removed and menthol formed by saponification. The menthol is then all transformed to the ester by the action of acetic anhydride and sodium acetate. This compound is then saponified back to menthol, and the amount of alkali consumed gives the amount of menthol by the above calculation.

REFERENCES.—United States Pharmacopœia; United States Dispensatory; Gildemeister and Hoffmann: "The Volatile Oils."

PEPPERMINT, SPEARMINT AND WINTERGREEN EXTRACTS

Alcohol.—Since these extracts usually contain only a small amount of oil,* the alcohol can in most cases be calculated from

* The Federal Standard (*U. S. Dept. Agr., Circ.* 136) requires not less than 3% of the essential oil in each of these extracts.

the sp. gr. of the extract. The method of calculation is described under Cassia Extract (p. 651). For the sp. gr. of the oil (the value *O* in the formula) use the following figures:

Peppermint oil	0.91
Spearmint oil	0.92
Wintergreen oil	1.18

If the extract is high in solids, determine the alcohol as follows:

Add 25 cc. of the extract to 75 cc. of a saturated solution of NaCl in a separatory funnel and extract twice with 50-cc. portions of petroleum ether (b. p. 40–60° C.). Collect the petroleum ether extract in a second separatory funnel and wash twice with two separate 25-cc. portions of saturated brine. Combine the original salt solution with the washings, add a little powdered pumice, and distill into a 100-cc. volumetric flask. When almost 100 cc. have been distilled, make up to the mark at a definite temperature and determine the alcohol from the sp. gr., as described on page 651.

NOTE.—A 50% solution of $CaCl_2$ may be used in place of saturated brine.

Oil (Modified Howard Method).—Pipette 10 cc. of the extract into a Babcock milk (not cream) bottle, add 1 cc. of CS_2, mix thoroughly, and then add 25 cc. of cold water and 1 cc. of conc. HCl. Close the mouth of the bottle and shake vigorously. Centrifugalize for 6 minutes and remove all but 3–4 cc. of the supernatant liquid, which should be practically clear, by aspirating through a glass tube of small bore. Connect the stem of the bottle with a filter pump, immerse for 3 minutes in water kept at about 70° C., remove from the bath every 15 seconds and shake vigorously. Continue in the same manner for 45 seconds, using a boiling water bath. Remove from the bath and shake while cooling. Disconnect from the suction and fill the bottle to the neck with saturated NaCl solution at room temperature. Centrifugalize for 2 minutes and read the volume of the separated oil from the top of the meniscus. Multiply the reading by 2 to obtain the percentage of oil by volume.

In the case of wintergreen use as a floating medium a mixture of 1 volume of conc. H_2SO_4 and 3 volumes of saturated Na_2SO_4 solution.

Methyl Salicylate in Wintergreen Extracts (Modified Hortvet and West Method).—Mix 10 cc. of the extract with 10 cc. of 10% KOH solution. Heat on the steam bath until the volume is reduced about $\frac{1}{2}$. Add a distinct excess of dil. HCl (1:1), cool and extract with 3 portions of ether, 40, 30 and 20 cc., respectively. Filter the extract through a dry filter into a weighed dish. Wash the paper with 10 cc. of ether and allow the filtrate and washings to evaporate spontaneously. Dry in a desiccator containing H_2SO_4 and weigh. Multiply the weight of salicylic acid thus found by 9.33 to obtain the percentage by volume of wintergreen oil in the sample. (Sp. gr. of wintergreen oil = 1.178.)

REFERENCE.—Association of Official Agricultural Chemists: "Methods of Analysis," 359 (1925).

VANILLA EXTRACT

Specific Gravity.—Determine at 20° C. with a pycnometer.

Alcohol.—Weigh into a distilling flask 20–25 grams of the sample and dilute with 100 cc. of water. Distill into a 100-cc. volumetric flask through a vertical condenser, stopping the distillation just short of 100 cc. Make up to volume at standard temperature and determine the sp. gr. of this distillate accurately with a pycnometer at the same temperature. Determine the percentage of alcohol by weight and by volume, as described on page 651.

Vanillin and Coumarin.*—The determination of vanillin, coumarin, normal lead number and residual color in the filtrate are all to be made on one portion, using 50 cc. of the sample. For the determination of vanillin and coumarin employ the modified Hess and Prescott method as follows:

VANILLIN.—Pipette 50 cc. of the extract at 20° C. into a 250-cc. beaker with marks showing volumes of 80 and 50 cc. Dilute to 80 cc. and evaporate to 50 cc. in a water bath kept at 70° C. or below. Dilute again to 80 cc. with water and evaporate to 50 cc. Transfer to a 100-cc. volumetric flask, rinsing the beaker with hot water, add 25 cc. of 8% neutral lead acetate solution, make up to the mark with water, shake, and let stand 18 hours (over-

* This method is not applicable to concentrated vanillin and coumarin preparations in which the amount of vanillin and coumarin present in 50 cc. exceeds the quantity dissolved in 100 cc. of water at 20° C. In such cases use a smaller quantity of the sample and dilute to 50 cc.

night) at 37–40° C. This can best be obtained by means of an incubating oven. Decant on a small, dry filter.

Pipette 50 cc. of the filtrate into a separatory funnel and extract four times, using successive 15-cc. portions of ether which has been washed twice with an equal volume of water to remove alcohol. Wash the combined ether solutions four or five times with dil. NH_4OH (1:11), using 10 cc. the first time and 5 cc. thereafter. Save the ether solution for the determination of coumarin.

Slightly acidulate the combined ammoniacal solutions with dil. HCl (1:2), cool and extract in a separatory funnel with 4 portions of washed ether, using about 40 cc. in all. Evaporate the ethereal solutions at room temperature, dry over conc. H_2SO_4 (more quickly accomplished in a vacuum desiccator) and weigh.* If the residue, after standing in a desiccator, is considerably discolored or gummy, re-extract in the dry state with boiling petroleum ether (b. p. 40° C. or below) not less than fifteen times; evaporate the solvent from the combined extracts, dry and weigh. The residue should now be white, crystalline vanillin with a m.p. of approximately 80° C. A small amount of this residue dissolved in 2 drops of conc. HCl, upon the addition of a crystal of resorcinol, should develop a pink color.

Coumarin.—Evaporate the original ether extract of the sample, after removal of the vanillin with NH_4OH, at room temperature, dry over conc. H_2SO_4 and weigh. The residue, if pure coumarin, should melt at approximately 67° C., and should respond to Leach's test for coumarin as follows: A small portion of the residue dissolved in not more than 0.5 cc. of hot water should develop a brown precipitate upon the addition of a few drops of 0.1 N iodine solution. This precipitate finally gathers in green flocks, leaving a clear brown solution. The reaction is especially marked if the reagent is applied with a glass rod to a few drops of the solution on a white plate or tile.

Lead Number (Winton).—To an aliquot of 10 cc. of the filtrate from the lead acetate precipitate obtained above, add 15 cc. of water, 10 cc. of dil. H_2SO_4 (1:9), and 100 cc. of 95% alcohol. Let stand overnight, filter on a weighed Gooch crucible, wash

* The vanillin residue often appears first in the form of oil-like droplets, which on standing crystallize into light-colored masses.

with 95% alcohol, dry at a moderate heat and ignite at low redness for 3 minutes, taking care to avoid the reducing flame. (It is best to place the Gooch crucible inside a platinum crucible during the ignition.) Cool in a desiccator and weigh. Conduct a blank determination, using water containing 4 or 5 drops of glacial acetic acid instead of the sample. Calculate the lead number from the following formula:

$$P = \frac{100 \times 0.6833(S - W)}{5} = 13.666(S - W).$$

In the above formula P = Lead Number (grams of metallic Pb in the precipitate from 100 cc. of the sample); S = grams of $PbSO_4$ corresponding to 2.5 cc. of the standard lead acetate solution as determined in the blank analysis; and W = grams of $PbSO_4$ in 10 cc. of the filtrate from the lead acetate precipitate as just described.

Color Value.—Pipette 2 cc. into a 50-cc. volumetric flask and make up to the mark with a mixture of equal parts of 95% alcohol and water. Determine the color value of this diluted extract in terms of red and yellow by means of the Lovibond tintometer, using the 1-inch cell. To obtain the color value of the original extract multiply the figures for each color by 25.

Residual Color after Precipitation with Lead Acetate.—Determine the color value in terms of red and yellow of a portion of the filtrate from the lead acetate precipitate obtained in the determination of vanillin and coumarin, using a 1-inch Lovibond cell. Multiply the reading by 2 to reduce the results to the basis of the original extract. If the actual reading of the solution is greater than 5 red and 15 yellow, as may happen if the extract is highly colored with caramel, use the 0.5- or 0.25-inch cell and multiply the readings by 4 or by 8, respectively.

Divide the figures for red and yellow, respectively, by the corresponding figures obtained by measurement of the original extract and multiply the quotients by 100, to obtain the percentages of the 2 colors remaining in the lead acetate filtrate.

Calculate also the ratio of red to yellow in both extract and lead filtrate.

Color Insoluble in Amyl Alcohol (Marsh Test).—Pipette 25 cc. of the extract into a porcelain dish and evaporate just to dryness on the steam bath. Transfer to a 50-cc. volumetric flask by means of 95% alcohol and water, using a total of 26.3 cc. of

95% alcohol. Dilute to the mark with water. Transfer 25 cc. of this solution to a separatory funnel. Add 25 cc. of the Marsh reagent and shake lightly to avoid emulsification. Let the layers separate and repeat the shaking and standing twice again. After the layers have separated clearly, run off the lower aqueous layer containing the caramel into a 25-cc. cylinder and make up the volume with 50% (by volume) alcohol. Compare this solution in a colorimeter with the remaining 25 cc. and express the results as percentage of Color Insoluble in Amyl Alcohol.

Marsh Reagent.—Mix 100 cc. of pure amyl alcohol, 3 cc. of sirupy H_3PO_4 and 3 cc. of water. Shake immediately before using. If the reagent becomes colored on standing, the amyl alcohol should be redistilled over 5% H_3PO_4 solution.

Total Solids.—Determine the total solids on 10 cc. of the sample by evaporating in a dish containing a weighed amount of quartz sand, as described on page 560.

Ash.—Evaporate 10 cc. of the extract, char and ignite until free from carbon at the lowest possible heat, not exceeding dull redness.

Sucrose.—Determine sucrose by polarization before and after inversion with HCl as described in the method for Reducing Sugars and Sucrose (p. 548), or by determining reducing sugars before and after inversion (Munson and Walker method) as described under Chemical Method (p. 550).

Vanilla Resins (Qualitative Tests).—Evaporate 50 cc. of the extract in a glass dish on a water bath until the alcohol is removed and make up to about the original volume with hot water. If alkali has not been used in the manufacture, the resins will appear as a flocculent red to brown residue. Acidify with dil. acetic acid (1:9), let stand a short time, collect the resins on a filter, wash with water and reserve the filtrate for further tests.

Place a portion of the filter with the attached resins in a few cc. of 5% KOH solution. The resins are dissolved, giving a deep red solution. Acidify, and the resins are reprecipitated.

Dissolve a portion of the resins in 95% alcohol. To 1 fraction add a few drops of 10% $FeCl_3$ solution; no striking coloration should be produced. To another portion add conc. HCl; little change in color should result. Most foreign resins, however, give color reactions.

To a portion of the filtrate obtained above, add a few drops of lead subacetate solution.* A very bulky precipitate should result, almost solid, and the filtrate from this precipitate should be practically colorless.

Test another portion of the filtrate from the resins for tannin with a solution of gelatin. Tannin should be present in varying but small quantities, but should not be present in great excess.

Glycerol.—Heat to boiling in a flask 100 cc.† of the extract and treat with successive small portions of milk of lime (containing about 15% of CaO) until it becomes first darker and then lighter in color. When cool add 200 cc. of 95% alcohol, let the precipitate subside, filter, and wash with 95% alcohol. Evaporate the filtrate in a porcelain dish on the water bath to about 10 cc. and proceed as in the determination of Glycerol in Lemon Extract (p. 654).

NOTES.—(1) This method embodies the methods and recommendations of the Association of Official Agricultural Chemists.

(2) The limits of composition of pure standard vanilla extracts as set forth in *Bur. of Chem., Bull.* 163, p. 89 are as follows:

(*a*) Percentage of vanillin should be not less than 0.10 nor more than 0.35.

(*b*) Normal lead number should be not less than 0.40 nor more than 0.80.

(*c*) The percentage of color insoluble in acidified amyl alcohol (Marsh's reagent) should be not more than 35 and will seldom exceed 25%.

* Basic lead acetate solution used for clarifying sugar solutions (see p. 546).

† The amount of glycerol in the sample taken for analysis should be between 0.10 and 0.40 gram.

CHAPTER XI

ANALYSIS OF WATER, SEWAGE, AND SOILS

SANITARY ANALYSIS OF WATER AND SEWAGE

General.—Before making a sanitary analysis of a sample of water, the general characteristics of the water should be noted. All substances which are likely to undergo change should be determined as quickly as possible. This includes free and albuminoid ammonia, nitrites, nitrates and oxygen consumed (also free CO_2 and alkalinity or acidity when desired).

The determinations included in the usual sanitary water analysis are given below and the form of reporting and the number of significant figures to be reported are also indicated:

Sediment	X.X
Turbidity (U. S. Geological Scale)	X.X
Odor	
Color (Platinum-cobalt Standard)	X.X
	Parts per 100,000
Residue on evaporation	X.XX
Nitrogen as:	
Free ammonia	X.XXXX
Albuminoid ammonia	X.XXXX
Nitrites	X.XXXX
Nitrates	X.XXXX
Oxygen consumed	X.XX
Total chlorine	X.XX
Hardness	X.X
Iron	X.XXXX

Odor.—The observation of the odor of cold and hot samples of surface waters is very important, as the odors are usually connected with some organic growths or with sewage contamination, or both. The odor of ground waters is often caused by the earthy constituents of the water-bearing strata. The odor of a con-

taminated well water is often a contributary evidence of its pollution.

Cold Odor.—Shake the sample violently in 1 of the gallon collecting bottles, about $\frac{1}{2}$ or $\frac{2}{3}$ full of the water at room temperature (about 20° C.). Remove the stopper and smell the odor at the mouth of the bottle.

Hot Odor.—Pour about 150 cc. of the sample into a 500-cc. Erlenmeyer flask. Cover the flask with a well-fitting watch glass, place on a hot plate and bring the water to just below boiling. Remove the flask from the plate and let it cool for not more than 5 minutes. Then shake with a rotary movement, slip the watch glass to one side and note the odor.

Expression of Results.—Express the quality of the odor by some such descriptive term as the following: vegetable, aromatic, grassy, fishy, earthy, moldy, musty, disagreeable, peaty, sweetish, sulfide, etc.

Sediment and Suspended Matter.—Ordinarily the sediment may be expressed qualitatively as slight, flocculent, considerable, or heavy. If quantitative results are desired, filter a measured quantity of the water after shaking (500 cc. are suitable) through a filter paper which has previously been dried in a weighing bottle in the oven at 105° C. to constant weight. Then dry the filter containing the sediment to constant weight, at the same temperature. To avoid absorption of moisture by the dry filter, make all weighings with the bottle stoppered. This gives the total suspended matter. If the mineral suspended matter is desired, ignite in a platinum crucible and weigh.

Note.—The difference between the total solids determined on filtered and unfiltered portions of the sample may also be used as a measure of the amount of suspended matter.

Turbidity.—The turbidity is due to suspended matter such as clay, silt, finely divided organic matter, microscopic organisms, etc. The standard of turbidity adopted by the U. S. Geological Survey is a water which contains 100 parts of silica per million in such a state of fineness that a bright platinum wire, 1 mm. in diameter, can just be seen when the center of the wire is 100 mm. below the surface of the water and the eye of the observer is 1.2 meters (about 4 feet) above the wire; the observation being made in the middle of the day, in the open air but not in sunlight,

and in a vessel so large that the sides do not shut out the light. The turbidity of such a water is arbitrarily fixed at 100.

The number obtained by dividing the weight of suspended matter in the sample, in parts per million, by the turbidity, is called the *Coefficient of Fineness*. If the coefficient is greater than 1, the matter in suspension is coarser than the standard; if less than 1, it is finer.

Silica Standards.—To prepare the standard, dry precipitated fuller's earth and sift it through a 200-mesh sieve. One gram of this preparation in 1 liter of distilled water makes a stock suspension containing 1000 parts of silica per million, which should have a turbidity of 1000. Test this suspension, after diluting a portion of it with nine times its volume of distilled water, by the platinum wire method, as described below, to ascertain if the silica has the necessary degree of fineness and if the suspension has the necessary degree of turbidity. If not, correct by adding more fuller's earth or more water as required.

Prepare standards for comparison from the stock suspension by diluting with distilled water. For turbidity readings below 20, keep standards of 0, 5, 10, 15, and 20 in clear bottles of the same size as are used in collecting the samples. For readings above 20, keep standards of 20, 30, 40, 50, 60, 70, 80, 90, and 100 in 100-cc. Nessler tubes approximately 20 mm. in diameter. In comparing the water under examination with the standards, take an amount equivalent to the standard, view the liquids sidewise towards the light, looking at some object, and note the distinctness with which the margins of the object may be seen. Keep the standard stoppered and shake both sample and standard thoroughly before making the comparison.

Note.—In order to prevent growth of bacteria or algæ in the standards, a small amount of mercuric chloride may be added to them.

Platinum Wire Method.—The platinum wire method of determining turbidity may be used directly on the sample instead of preparing standards as above. It is the method to be used in ascertaining the correctness of the stock suspension above described.

This method requires a rod with a platinum wire of 1-mm. diameter (0.04 inch, No. 18 B. & S. gage) inserted in it about 1 inch from one end of the rod and projecting from it at least 25

mm. at a right angle. Near the other end of the rod, at a distance of 1.2 meters (about 4 feet) from the platinum wire, place a wire ring directly above the wire. When making the examination look through this ring with the eye directly above it. Graduate the rod as follows: At a distance of 100 mm. from the center of the wire, mark 100. If desired, other graduations may be made according to Table XXVI below or the distance may be measured in mm. and the turbidity calculated.

TABLE XXVI—GRADUATION OF TURBIDITY ROD FOR TESTING WATER

Turbidity, Parts per Million	Vanishing Depth of Wire, Mm.	Turbidity, Parts per Million	Vanishing Depth of Wire, Mm.
7	1059	70	138
8	971	75	130
9	983	80	122
10	794	85	116
11	729	90	110
12	674	95	105
13	627	100	100
14	587	110	93
15	551	120	86
16	520	130	81
17	493	140	76
18	468	150	72
19	446	160	68.7
20	426	180	62.4
22	391	200	57.4
24	361	250	49.1
26	336	300	43.2
28	314	350	38.8
30	296	400	35.4
35	257	500	30.9
40	228	600	27.7
45	205	800	23.4
50	187	1000	20.9
55	171	1500	17.1
60	158	2000	14.8
65	147	3000	12.1

Procedure.—Lower the rod vertically into the water as far as the wire may be seen, and then read the level of the surface of the water on the graduated scale (or mark the point and measure the distance). The following precautions must be taken to insure correct results:

Observations must be made in the open air, preferably in the middle of the day and not in direct sunlight. The wire must be kept bright and clean. If for any reason observations cannot be made under natural conditions directly, a pail or tank may be filled with water and the observation taken in that, but in this case care must be taken that the water is thoroughly stirred before the observation is made, and no vessel is to be used for this purpose unless its diameter is at least twice as great as the depth to which the wire is immersed. Waters which have a turbidity above 500 must be diluted with clear water before the observations are made; but if this is done, the degree of dilution must be reported.

The wire method is to be used for testing the degree of fineness of the silica standard, and this should be such that when added to distilled water in an amount equal to 100 parts per million, the wire observed under standard conditions can be just seen at a depth of 100 mm. below the surface of the water.

Recording of Results.—Record results of turbidity observations as follows:

Turbidity between	Record to nearest
1 and 50	1
51 and 100	5
101 and 500	10
501 and 1000	50
1001 and greater	100

Color.—The "true color" of water is considered that part of the apparent color which is due only to substances in solution, *i.e.*, it is the color of water after filtration. The "apparent color" is the color as viewed by inspection of the original sample. In stating the results, the word "color" means the color of the filtered sample, unless otherwise expressed.

Platinum-cobalt Standard.—The platinum-cobalt method of measuring color is the standard and the unit of color is that produced by one part of Pt per million. The ratio of Co to Pt may be varied to match the shade in special cases. The proportion given below is usually satisfactory.

Prepare the standard solution (which has a color of 500) as follows: Dissolve in water 1.245 grams of K_2PtCl_6 (containing 0.5 gram of Pt), 1 gram of crystallized $CoCl_2 \cdot 6H_2O$ (containing 0.25 gram of Co) and 100 cc. of conc. HCl, and dilute with distilled water to 1 liter. Place varying aliquots of this solution in Nessler tubes and dilute with distilled water to the 50-cc. or 100-cc. mark. These diluted solutions should have colors of 0, 5, 10, 15, 20, 25, 30, 35, 40, 50, 60, and 70, respectively. The tubes must be of such size that the 50-cc. mark is between 20 and 25 cm. above the bottom and is uniform for all tubes. Protect these standard tubes from dust and from evaporation when not in use.

Procedure.—Fill a clean Nessler tube with the sample to the height equal to that in the standard tubes, and compare the color with the standards. The observation must be made by looking vertically downward through the tubes upon a white surface placed at such an angle that light is reflected upward through the column of liquid. Estimate the color of the water from the standards which most nearly match it.

Notes.—(1) Waters that have a color darker than 70 must be diluted with distilled water before making the comparison.

(2) Water containing suspended matter must be filtered until no visible turbidity remains before the observation is made. If the suspended matter is coarse, use filter paper; if fine, a Berkefeld filter is recommended. The Pasteur filter must not be used, as it has a decolorizing effect.

Recording of Results—Record results of color determinations as follows:

Color between	Record to Nearest
1 and 50	1
51 and 100	5
101 and 250	10
251 and 500	20

Dissolved Oxygen.—See page 703.

Chemical Analysis.—Express results of chemical analysis in parts per 100,000.

Residue on Evaporation (Total Solids).—Evaporate 100 cc. of the sample in a weighed platinum dish on the water bath. If the water has a high Mg content, add 25 cc. of 0.02 N Na_2CO_3 solution,* correcting for this in the final calculation. Dry the residue for 1 hour at a temperature of about 105° C. Cool in a desiccator over conc. H_2SO_4 and weigh. Repeat until there is no further loss in weight. With highly mineralized waters it is preferable to use a temperature of 180° C.

Loss on Ignition.—Heat the platinum dish with the residue in a "radiator," which consists of another platinum or nickel dish large enough to allow an air space of about 0.5 inch between the inner and outer dishes, the inner dish being supported by a triangle of platinum wire laid on the bottom of the outer dish. Suspend over the inner dish a disc of nickel or platinum foil large enough to cover the outer dish and radiate heat upon the residue. Heat the large dish to bright redness until the residue is white or nearly so. Let cool, moisten the residue with a few drops of distilled water, dry in the oven for ½ hour, cool and weigh. The difference between this and the total solids is the Loss on Ignition.

Notes.—(1) An electric muffle furnace may be used in place of the radiator.

(2) It is not customary to report the loss on ignition but it is of value in interpreting the analysis. The manner in which the residue behaves as to odor and color upon ignition should be noted, as it often gives a helpful clue to the character of the organic matter.

Nitrogen as Free Ammonia

General.—There are 2 methods for estimating nitrogen present as free ammonia: (I) by distillation, and (II) by direct nesslerization. The former is recommended for most waters, while the latter is preferable for sewages, sewage effluents, and highly polluted surface waters, or waters containing H_2S.

I. Free Ammonia by Distillation.—Connect a 1-liter round-bottomed flask to a vertical block-tin or aluminum condenser in

* This prevents the hydrolysis of $MgCl_2$ and loss of HCl.

such a way that the distillate will drop directly into the Nessler tubes. Free the apparatus from NH_3 by boiling distilled water in it until the distillate shows no further traces of free NH_3. Then empty the distilling flask and measure into it 500 cc. of the sample, or a smaller portion diluted to 500 cc. with NH_3-free water. Apply the heat so that the distillation will be at the rate of 6–10 cc. per minute. Collect 4* Nessler tubes of the distillate, 50 cc. to each portion. These contain the free NH_3, to be measured as described below.

NOTE.—If the sample is acid to methyl orange or if the presence of urea is suspected, add about 0.5 gram of Na_2CO_3 previous to distillation. Omit this when possible as it tends to increase bumping. Use only Nessler tubes which do not show a variation of more than 6 mm. (0.25 inch) in the distance of the 50-cc. graduation mark from the bottom. The tubes must be of clear, colorless glass with polished bottoms.

The comparison of the distillates may be made either (1) against nesslerized solutions containing known quantities of N as NH_4Cl or (2) against permanent standard solutions in which the colors of nesslerized standard ammonia colors are duplicated by solutions of Pt and Co chlorides.

(1) Comparison with Ammonia Standards.—REAGENTS.—For comparison with ammonia standards, prepare the following reagents:

(*a*) *Ammonia-free Water.*

(*b*) *Standard NH_4Cl Solution.*—Dissolve 3.82 grams of NH_4Cl in 1 liter of NH_3-free water and dilute 10 cc. of this to 1 liter with NH_3-free water. 1 cc. of the final solution equals 0.00001 gram of N, equivalent to 0.00001216 gram of NH_3.

(*c*) *Nessler's Reagent.*—Dissolve 50 grams of KI in a minimum quantity of cold NH_3-free water (about 35 cc.). Add a saturated solution of $HgCl_2$ until a slight permanent precipitate forms. Add 400 cc. of 50% KOH solution or 35% NaOH solution made by dissolving the caustic and allowing it to settle clear before using. Then dilute to 1 liter, let settle till clear and decant. This solution should give the required color with ammonia

* If the free NH_3 is unusually high, it may be necessary to collect more than 4 tubes of distillate. The last tube should be free or practically free from NH_3

within 5 minutes after addition and should not precipitate with small amounts of NH_3 within 2 hours.

PROCEDURE.—Prepare a series of 16 Nessler tubes which contain the following volumes of the standard NH_4Cl solution, diluted to 50 cc. with NH_3-free water, namely, 0.0, 0.1, 0.3, 0.5, 0.7, 1.0, 1.4, 1.7, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 and 6.0 cc. These will contain 0.00001 gram of N for each cc. of the standard solution used.

Nesslerize the standards and also the 4 distillates from the sample by adding 1 cc. of Nessler's reagent to each tube. Do not stir the contents of the tubes. Have the temperature of the tubes practically the same as that of the standard, otherwise the colors will not be directly comparable. Let the tubes stand for at least 10 minutes after nesslerizing. Compare the color produced in these tubes with that of the standards by looking vertically downward through them at a white surface placed at an angle in front of the window so as to reflect the light upwards.

In case the color obtained by nesslerizing the distillates is greater than that of the darkest standard, mix the contents of the tube thoroughly and pour out $\frac{1}{2}$. Dilute the remainder to the original volume with NH_3-free water. Then make the color comparison and multiply the result by 2. If the color is still too dark, repeat the process of division until a reading can be made. If the color of the distillates is too high, this process may be shortened by mixing together all of the distillates in one sample before making the comparison, then taking an aliquot portion for comparing with the standards.

If a precipitate is formed, dilute the reagent before adding it to the tubes.

After the readings have been made and recorded, add together the results obtained on separate tubes of the sample to get the total number of cc. of standard required. If 500 cc. of the sample were distilled, multiply this sum by 0.002 to get the parts of N as free NH_3 per 100,000 parts of the sample.

(2) **Permanent Standards.**—Permanent standards for comparison may be prepared as below and the colors of the nesslerized distillates compared with these after the former have stood about 10 minutes.

REAGENTS.—(1) *Platinum Solution.*—Dissolve 2 grams of K_2PtCl_6 in a small amount of water, add 100 cc. of conc. HCl and dilute to 1 liter.

(2) *Cobalt Solution.*—Dissolve 12 grams of $CoCl_2 \cdot 6H_2O$ in water, add 100 cc. of conc. HCl and dilute to 1 liter.

PROCEDURE.—For the standards place varying amounts of these two solutions in Nessler tubes and fill up to the 50-cc. mark with distilled water as shown in Table XXVII.

The amounts there stated are approximate, and the actual amount necessary will vary with the character of the Nessler solution used, with the color sensitiveness of the analyst's eye, and with the other incidental conditions. The final test of the standard is best obtained by comparing it with nesslerized standards and modifying the tint accordingly. Such a comparison should be made for each new batch of Nessler solution and should be checked by each analyst.

TABLE XXVII—PERMANENT STANDARDS FOR NH_3 DETERMINATION

Equivalent Volume of Standard NH_4Cl Solution, *cc.*	Platinum Solution, *cc.*	Cobalt Solution, *cc.*
0.0	1.2	0.0
0.1	1.8	0.0
0.2	2.8	0.0
0.4	4.7	0.1
0.7	5.9	0.2
1.0	7.7	0.5
1.4	9.9	1.1
1.7	11.4	1.7
2.0	12.7	2.2
2.5	15.0	3.3
3.0	17.3	4.5
3.5	19.0	5.7
4.0	19.7	7.1
4.5	19.9	8.7
5.0	20.0	10.4
6.0	20.0	15.0
7.0	20.0	22.0

It is necessary to use tubes of the same size and graduations as those used to collect the water distillates. These standards may be kept for several months if protected from dust. The method of calculating results is the same as with the ammonia standards.

II. Free Ammonia by Direct Nesslerization.—Reagents.—Prepare the following solutions with NH_3-free water:

(*a*) *$CuSO_4$.*—10% (crystals).

(*b*) *Lead Acetate.*—10%.

(*c*) *NaOH or KOH.*—50%.

(*d*) *$ZnSO_4$.*—Saturated solution.

Procedure for Water.—Mix 50 cc. of the sample in a glass-stoppered graduate with an equal volume of NH_3-free water, and add a few drops of the $CuSO_4$ solution. After thoroughly mixing, add 1 cc. of the caustic solution and again thoroughly mix. Let stand for a few moments. A heavy precipitate should fall, leaving a colorless, supernatant liquid. Nesslerize an aliquot portion of this clear liquid, compare with standards and compute the amount of N as free NH_3, as described under the Distillation Method.

Samples containing H_2S may require addition of a few drops of lead acetate or $ZnSO_4$ solution in addition to the $CuSO_4$. Samples high in Mg may often be clarified by addition of the caustic alone.

Procedure for Sewage.—Add 1 cc. of the $CuSO_4$ solution to 100 cc. of the sample in a glass-stoppered bottle or cylinder, mix well, add 1 cc. of the caustic solution, again mix well and let settle. If the supernatant liquid does not become perfectly clear, take a fresh sample and add the alkali first and then the $CuSO_4$. If the sample contains H_2S, add first 1 cc. of lead acetate solution and then 1 cc. of the alkali. If this fails to clarify, take a fresh portion and add first 1 cc. of the $ZnSO_4$ solution and then 1 cc. of the alkali.

Place 5 cc. or less of the clarified liquid in a 50-cc. Nessler tube, dilute to the mark with NH_3-free water, nesslerize and compare with standards.

Nitrogen as Albuminoid Ammonia

General.—The addition of an alkaline permanganate solution to liquids containing nitrogenous organic matter causes the for-

mation of NH_3, the amount of which can be measured upon distillation of the treated sample and nesslerization of the distillate. In sewages and other liquids and substances containing considerable nitrogenous organic matter, the percentage of nitrogenous material which is ammonia-forming is decidedly variable. For this reason albuminoid NH_3 results in such cases are less valuable than the total organic N, sometimes called the Kjeldahl nitrogen. Hence, for sewage work, including the analyses of both the influents and the effluents of purification plants, as well as the study of highly polluted streams, it is recommended that albuminoid NH_3 determinations be omitted and in their place the total organic N be determined.

For ground waters and surface waters containing but little pollution, the N as albuminoid NH_3 quite uniformly approximates about one-half of the total organic N. Accordingly the continuance of albuminoid NH_3 determinations for this class of work is approved. Nevertheless the inferiority of such results to those of total organic N is recognized.

Reagent.—*Alkaline $KMnO_4$.*—Pour 1200 cc. of distilled water in a 2.5-liter porcelain dish, boil 10 minutes and turn off the gas. Add 16 grams of $KMnO_4$ and stir until dissolved. Then add 800 cc. of a 50% clarified solution of KOH (or 35% NaOH solution) and enough NH_3-free water to make 2500 cc. Boil down to 2000 cc. Test each batch of this solution for albuminoid NH_3 by making a blank determination on 50 cc. and correct for this blank in the analysis.

Procedure.—Interrupt the distillation (made as already described) after the collection of the distillate for free NH_3, add 50 cc. or more of the alkaline $KMnO_4$ and continue the distillation until at least 4 (preferably 5) 50-cc. portions of the distillate have been collected in separate tubes. Have enough permanganate solution present to insure the maximum oxidation of the organic matter. Determine the N in the distillates by nesslerization as previously described and express the results in terms of Nitrogen as Albuminoid Ammonia in parts per 100,000.

NOTES.—(1) Dissolved N as albuminoid NH_3 may be determined from a sample from which suspended matter has been removed by filtration either through filter paper, or, if finely divided matter is present, through a Berkefeld filter.

(2) Suspended N as albuminoid NH_3 may be obtained by taking the difference between the total and dissolved N.

Total Organic Nitrogen

Procedure for Water.—Boil 500 cc. of the sample in a round-bottomed flask until free from NH_3. This usually requires the distillation of about 200 cc. of the sample, which may be collected for the determination of free NH_3.

Add 5 cc. of conc. H_2SO_4, free from N, together with a small piece of ignited pumice. Mix by shaking and place over a flame under a hood. Digest until copious fumes of SO_3 are given off and the liquid chars and finally becomes colorless or pale straw color. If necessary the digestion temperature may be raised by the addition of 5 grams of anhydrous K_2SO_4 or Na_2SO_4. Cool, dilute to about 300 cc. with NH_3-free water and add an excess of 10% ammonia-free NaOH solution. Distill off the NH_3, collect in Nessler tubes, nesslerize and compare with standards as already described.

Procedures for Sewage.—For sewages containing less than 5 parts of organic N per 100,000 Method I is satisfactory. For greater concentrations Method II is more accurate.

Method I.—Measure 100 cc. or less of the sample into a 500-cc. Kjeldahl flask and distill off the free NH_3. Add 10 cc. of conc. H_2SO_4, 1 cc. of 10% $CuSO_4$ solution, and 5 grams of anhydrous, powdered Na_2SO_4 or K_2SO_4. Digest under the hood over a low flame for 30 minutes after the liquid has become colorless. Partially cool and dilute to about 250 cc. with NH_3-free water. Add a few drops of phenolphthalein and then add 50% NaOH solution, carefully, until alkaline. Immediately connect with a condenser which has been steamed out and distill the NH_3 into Nessler tubes. Nesslerize the distillate and compare with standards as described under Free Ammonia.

Correct the total N found by a blank determination made with the same amounts of reagents as were used in the analysis.

Method II.—Using at least 100 cc. of the sample, proceed as under Method I, collecting the distillate in 25 cc. (or more) of 0.05 N H_2SO_4 or HCl containing 3 drops of a 1% solution of methyl red in alcohol. Collect about 200 cc. of distillate and titrate the excess of acid with 0.05 N NaOH. Calculate the amount

of N from the acid consumed, after correcting for the amount found in a blank determination on the reagents.

Calculation.—1 cc. 0.05 N acid = 0.0007 gram nitrogen.

Nitrogen as Nitrites

General.—The formation of nitrites is the second intermediate step by which nitrogenous matter passes from crude organic matter to mineral matter (nitrates). Nitrites are also formed continuously by the reduction of nitrates by bacterial action and consequently the determination must be made on fresh samples. The following is the standard method of procedure for water and sewages:

Reagents.—(1) *Sulfanilic Acid Solution.*—Dissolve 8.00 grams of the purest sulfanilic acid in 1000 cc. of 5 N acetic acid (sp. gr. 1.041). This is practically a saturated solution.

(2) *Alpha-amidonaphthalene Acetate Solution.*—Dissolve 5.0 grams of solid alpha-amidonaphthalene* in 1000 cc. of 5 N acetic acid and filter the solution through washed absorbent cotton.

(3) *$NaNO_2$ Stock Solution.*—Dissolve 1.1 grams of $AgNO_2$ in nitrite-free water; precipitate the Ag with NaCl solution and dilute the whole to 1 liter.

(4) *Standard $NaNO_2$ Solution.*—Dilute 100 cc. of solution (3) to 1 liter, then dilute 10 cc. of this solution to 1 liter with sterilized nitrite-free water, add 1 cc. of $CHCl_3$ and preserve in a sterilized bottle. 1 cc. = 0.0000001 gram N, or 0.000000329 gram NO_2.

(5) *Fuchsin Solution.*—0.1 gram of basic fuchsin per liter.

Procedure.—Measure out into a Nessler tube 100 cc. of the sample (decolorized if necessary by adding aluminum hydroxide free from nitrite—see under Chlorine), or a smaller portion diluted to 100 cc. The Nessler tubes must be of clear white glass, with the 100-cc. graduation marks not varying more than 6 mm. in distance above the bottom. At the same time make a set of standards by diluting various volumes of the standard nitrite solution in Nessler tubes to 100 cc. with nitrite-free water; for example, 0, 1, 2, 4, 7, 10, 14, 17, 20 and 25 cc. Add 2 cc. of reagents (1) and (2) above to the sample and to each standard. Mix well and let stand 10 minutes. Compare the sample

* Alpha-naphthylamine.

with the standards. Do not let the samples stand over ½ hour before being compared. Make a blank determination in all cases to correct for the presence of nitrite in the air, water, and reagents. If the color of the sample is deeper than that of the highest standard, repeat the test on a smaller portion diluted to 100 cc.

When 100 cc. of the sample are used, then 0.0001 times the number of cc. of the standard gives the parts of N as nitrite per 100,000 parts of water.

NOTES.—(1) The solution must be acid. HCl, which formerly was in quite general use in this country as a solvent for the naphthylamine, permits satisfactory results to be obtained, but the speed of the reaction is much slower than in the case of acetic acid. For this reason the latter acid is preferred.

(2) The nitrite standards made up as described above may, as an expedient in routine work, be matched by diluting the fuchsin reagent (5) to the required depth of color. For waters high in nitrite and for all sewage work, these fuchsin standards have been found to be sufficiently accurate. They should be checked once a month and if kept out of the bright sunlight are more permanent than the dilute nitrite standard.

(3) For cases not involving court testimony, the work can be considerably shortened by comparing the sample with colored squares of paper printed on a white background instead of with the standard nitrite tubes.

NITROGEN AS NITRATES

General.—No single method appears to be applicable to all classes of water and sewage and there is no method which is not subject to considerable error. Where the amount of Cl is less than 3 parts per 100,000, the phenoldisulfonic acid method is recommended; in other cases the reduction method, particularly in sewage work.

Phenoldisulfonic Acid Method (for Waters Low in Cl).—REAGENTS.—(1) *Phenoldisulfonic Acid.*—Dissolve 25 grams of pure white phenol in 150 cc. of conc. H_2SO_4 in a round-bottomed flask. Add 75 cc. of fuming sulfuric acid (15% free SO_3), stir well and heat for 2 hours at about 100° C.

(2) *KOH Solution.*—Dissolve about 675 grams of KOH in water and dilute to 1 liter. 10 cc. of this solution should neutralize about 4 cc. of the phenoldisulfonic acid.

(3) *Standard Nitrate Solution.*—Dissolve 0.722 gram of pure, recrystallized KNO_3 in 1 liter of nitrate-free distilled water. Evaporate cautiously 10 cc. of this strong solution to dryness on

the water bath in a porcelain dish. Moisten the residue quickly and thoroughly with 2 cc. of phenoldisulfonic acid, stirring with a small glass rod, and dilute to 1 liter for the standard solution. 1 cc. = 0.000001 gram N, or 0.00000443 gram NO_3.

PROCEDURE.—Evaporate 20 cc. of the sample in a small porcelain evaporating dish on the water bath, removing it from the bath just before it has come to dryness. Let the last few drops evaporate at room temperature in a place protected from dust. When the sample is suspected to contain a large amount of nitrate, evaporate less than 20 cc. If it is suspected to contain but little, evaporate more. If the sample has a high color, decolorize before evaporating by the use of washed $Al(OH)_3$, as directed under the determination of Chlorine (p. 686).

Add 2 cc. of phenoldisulfonic acid and rub this quickly and thoroughly over the residue with a glass rod. Add about 10 cc. of distilled water and stir with the glass rod until mixed. Add slowly the strong KOH solution until the maximum color is developed. Transfer the liquid to a 100-cc. Nessler tube (filtering if necessary) and fill the tube to the 100-cc. mark with distilled water.

If nitrates are present there will be formed a yellow color. Compare with standards made by putting the following quantities of the standard nitrate solution into 100-cc. tubes and making up to the 100-cc. mark with distilled water after adding 5 cc. of conc. KOH to each tube; namely, 0, 1, 2, 4, 7, 10, 15, 20, 25, 30, 35 and 40 cc. These standards may be kept for several weeks. Compare the sample, treated as above described, with these standards by looking down vertically through the tubes at a white surface so placed in front of a window that it will reflect the light upward through them.

Divide the figure (cc. of standard) obtained by this comparison by 10 times the number of cc. of the water evaporated. This will give parts per 100,000 of N in the form of nitrates.

NOTE.—If nitrite nitrogen is present in excess of 0.1 part per 100,000, add a few drops of dilute $KMnO_4$ solution to the sample until a faint pink color persists. Then determine the nitrate N and correct the result for the amount of N thus oxidized from nitrite to nitrate.

Reduction Method (for Waters and Sewage High in Cl). REAGENTS.—(1) *NaOH or KOH Solution.*—Dissolve 250 grams of

the caustic in 1250 cc. of water. Add several strips of Al foil and let the action proceed overnight. Boil down to 1 liter.

(2) *Aluminum Foil.*—Use strips of pure Al about 10 cm. long, 6 mm. wide and 0.33 mm. thick, and weighing about 0.5 gram.

Procedure.—Measure 100 cc. or less of the sample into a 300-cc. casserole. Add 2 cc. of the caustic solution and boil down to about 20 cc. Pour the contents of the casserole into a test-tube about 16 cm. long and 3 cm. in diameter and of about 100-cc. capacity. Rinse the casserole several times with N-free water and add the rinsings to the solution already in the tube, making the volume approximately 75 cc. Add a strip of Al foil, and close the tube with a rubber stopper through which passes a glass tube about 5 mm. in diameter, bent into a V. Make the short end of the tube flush with the lower side of the rubber stopper while the other end extends below the surface of distilled water contained in another test-tube. This apparatus serves as a trap through which the evolved hydrogen escapes freely. The amount of NH_3 escaping into the trap is slight and may be neglected. Let the action proceed for a minimum period of 4 hours, or overnight. Pour the contents of the tube into a distilling flask, dilute with 250 cc. of NH_3-free water, distill, collect the distillate in a 250-cc. volumetric flask and nesslerize an aliquot. If the supernatant liquid in the reduction tube is clear and colorless, the solution may be diluted to a definite volume and an aliquot nesslerized without distillation.

Oxygen Consumed

General.—"Oxygen consumed" means the oxygen which the organic compounds of sewage and water consume when treated in an acid solution with $KMnO_4$. It is also called "oxygen required" and "oxygen absorbed." It is the C and not the N in organic matter which is thus oxidized by $KMnO_4$. This determination is hence frequently referred to as an indication of the carbonaceous organic matter present. It indicates only a certain portion of the carbon, however, varying in different samples of water and of sewage. Furthermore, it does not directly differentiate the C present in unstable organic matter from that which might be called fairly stable organic matter, such as is sometimes referred to as residual humus matter. If nitrates, ferrous salts,

sulfides or other oxidizable mineral compounds are present, they will increase the O consumed and a correction should be made for them (see note 2, below).

The determination of oxygen consumed is an empirical procedure and details must be strictly followed to obtain concordant results. The method is not reliable with waters requiring a greater dilution than 1 : 1.

Reagents.—(1) *Dilute Sulfuric Acid.*—One volume of conc. H_2SO_4 to 3 of distilled water. This must be freed from oxidizable matters by adding $KMnO_4$ until a faint pink color persists after standing several hours.

(2) *Standard $KMnO_4$ Solution.*—Dissolve 0.4 gram of the crystals in 1 liter of distilled water. Standardize against the oxalate solution as follows: Add 10 cc. of the dil. H_2SO_4 and 10 cc. of the $KMnO_4$ solution to 100 cc. of distilled water and digest 30 minutes. Then add 10 cc. of the oxalate solution followed by $KMnO_4$ solution till a pink coloration appears. This destroys the oxygen-consuming capacity of the distilled water. Add another 10 cc. of the oxalate and titrate with the $KMnO_4$. Adjust the latter solution so that 1 cc. is equivalent to 1 cc. of the oxalate.

(3) *Ammonium Oxalate Solution.*—Dissolve 0.888 gram of $(NH_4)_2C_2O_4 \cdot H_2O$ in 1 liter of distilled water. 1 cc. = 0.0001 gram of oxygen. Instead of the $(NH_4)_2C_2O_4$ 0.788 gram of $H_2C_2O_4 \cdot 2H_2O$ or 0.837 gram of $Na_2C_2O_4$ may be used.

(4) *Sodium Hydroxide Solution.*—Dissolve 1 part of pure NaOH in 2 parts of distilled water.

Procedure.—Acid Digestion.—Measure into a flask 100 cc. of the water, or if high in organic content, a smaller portion diluted to 100 cc. Add 10 cc. of the H_2SO_4 solution and 10 cc. of the standard $KMnO_4$ solution and digest for exactly 30 minutes in a bath of boiling water, the level of which is kept above the level of the contents of the flask. Remove the flask, add 10 cc. of the oxalate solution and titrate hot with the $KMnO_4$ solution until a faint but distinct pink is obtained. (Accurate 10-cc. pipettes should be used for measuring the liquids.) Using 100 cc. of the water, $\frac{1}{10}$ of the difference between the volumes of $KMnO_4$ and oxalate solutions used, expressed in cc., gives Oxygen Consumed in parts per 100,000.

NOTES.—(1) If 10 cc. of the $KMnO_4$ is insufficient for complete oxidation, repeat the determination, using 15 cc. or more. There should be an excess of at least 5 cc. of the $KMnO_4$ when the oxalate is added.

(2) If the sample contains sulfides, nitrites, or ferrous salts in appreciable quantity, correct the oxygen-consumed figure for the $KMnO_4$ reduced by these as follows: Digest another 100-cc. portion of the water with 10 cc. (see note 1) of the $KMnO_4$ at room temperature for 3 minutes. Add about 1 cc. of 10% KI solution (free from iodates), mix well, and titrate the liberated iodine with a weak thiosulfate solution (1.0 gram per liter). Run a blank on 10 cc. of the $KMnO_4$ and 100 cc. of freshly distilled water in the same way to establish the relation between the $KMnO_4$ and the thiosulfate solution. The amount of $KMnO_4$ consumed by the 100 cc. of sample in the cold should be subtracted from the amount consumed hot, before calculating the Oxygen Consumed.

If the sample contains both oxidizable mineral compounds and gaseous organic compounds, the latter should be driven off by heat and the sample allowed to cool before determining the correction factor. The amount of the correction should be stated in the report.

ALKALINE DIGESTION.—For brines or waters high in Cl, digestion in alkaline solution is preferable to acid. The procedure is the same as for the Acid Digestion with the following exceptions: Add 0.5 cc. of the conc. NaOH solution and 10 cc. (see note 1, above) of the standard $KMnO_4$ to the sample and digest in a boiling water bath for 30 minutes. Then remove the flask, add 5 cc. of the dil. H_2SO_4 and 10 cc. of the standard oxalate and titrate with the $KMnO_4$ as above.

TOTAL CHLORINE

General.—Chlorine in waters and sewages has its origin for the most part in the common salt, which comes, generally speaking, from mineral deposits in the earth, from the ocean vapors carried inland by the wind, or from polluting materials like sewage and trade wastes, which contain the salt used in the household and in manufacturing. Comparison of the chlorine content of a water with that of other waters in the general vicinity known to be unpolluted, frequently affords useful information as to its sanitary quality.

Reagents.—(1) *Standard Salt Solution.*—Dissolve 16.49 grams of pure fused NaCl in water and dilute to 1 liter. Dilute 100 cc. of this stock solution to 1 liter to obtain a standard solution, each cc. of which contains 0.001 gram of Cl.

(2) *Standard $AgNO_3$ Solution.*—Dissolve 2.396 grams of $AgNO_3$ crystals in 1 liter of distilled water. One cc. of this will be equivalent to approximately 0.0005 gram of chlorine. Standardize against the standard salt solution, as described below under Procedure.

(3) *Potassium Chromate Indicator.*—Dissolve 50 grams of neutral K_2CrO_4 in a little water. Add enough $AgNO_3$ to produce a slight red precipitate. Let stand a day or two, filter and make up the filtrate to 1 liter with distilled water.

(4) *Aluminum Hydroxide.*—Dissolve 125 grams of potash alum or ammonia alum in 1 liter of water. Precipitate the $Al(OH)_3$ by cautiously adding NH_4OH. Wash the precipitate in a large jar by the successive addition of distilled water and by decantation until free from Cl, nitrites and NH_3.

Procedure.—Use 50 cc. of the sample in a white 6-inch porcelain evaporating dish, where the Cl is not extremely low or very high. If the Cl is very high, use 25 cc. (or even a smaller quantity), diluting the volume taken to 50 cc. with distilled water. A satisfactory end-point cannot be obtained when more than 8–10 cc. of the $AgNO_3$ solution are required. When there are over 100 parts of Cl per 100,000, a gravimetric determination should be made.

When the sample is very low in Cl more accurate results may be obtained by adding, prior to titration, 1 cc. of standard NaCl solution, correcting for this in the calculation. Or 250 cc. of the sample may be concentrated by evaporation to 50 cc.

If the sample has a color greater than 30, it must be decolorized by shaking it thoroughly with washed $Al(OH)_3$ (3 cc. to 500 cc. of the sample). Make the determination on an aliquot of the clarified sample, filtered if necessary.

Before titrating the Cl add 2 or 3 drops of phenolphthalein indicator. If a red color appears, neutralize with approximately 0.1 or 0.05 N H_2SO_4. If the water is acid to methyl orange, add a slight excess of pure $CaCO_3$ (or just neutralize with 0.1 or 0.05 N Na_2CO_3). If the sample contains H_2S, acidify with H_2SO_4, boil a few minutes, cool, neutralize with $NaHCO_3$ and dilute to the original volume.

Rotate the neutral liquid in the dish to make sure that no portion of any residue on the side walls remains undissolved, rubbing

if necessary with a rubber-tipped glass rod. Add 1 cc. of the K_2CrO_4 indicator and titrate with the $AgNO_3$ solution, under similar conditions as to volume, light and temperature as were used in standardizing the $AgNO_3$, until a faint reddish coloration is perceptible. The detection of the end-point is facilitated by frequent comparison of the contents of the porcelain dish in which the determination is being made with those of another dish placed alongside and containing the same quantity of chromate solution in 50 cc. of distilled water. It is also preferable to make the titrations in a darkened room provided with a yellow light.

Hardness

General.—The hardness of water is caused chiefly by the salts of Ca and of Mg. It is commonly measured by the soap-destroying power of the water. The addition of K or Na soap causes its decomposition and produces insoluble Ca and Mg soaps. The solubility of carbonates of Mg and Ca in a water beyond certain limits depends upon the presence of CO_2 and results in bicarbonates. On boiling the CO_2 is removed and the normal carbonates precipitated. Precipitation, however, is not complete, as the normal carbonates themselves have a slight solubility. The hardness of the water removed by boiling is called Temporary Hardness. The hardness which still remains is termed Permanent Hardness, and is due largely to sulfates and chlorides of Ca and Mg and to the traces of carbonates still held in solution.

It is generally sufficient to determine the total hardness of the water. In case the permanent hardness is also desired, boil gently a known volume of the water for $\frac{1}{2}$ hour, let cool, and then restore to its original volume with recently boiled and cooled distilled water. Then filter the water and determine the permanent hardness in the filtrate. This, subtracted from the total hardness, will give the temporary hardness.

Hardness is expressed in terms of $CaCO_3$. The most accurate method for total hardness is to calculate it from the chemical determinations of CaO and MgO in the water. (Iron and other metals must also be included if present in significant amounts.) The soap method gives a rough approximation of the true hardness, although it is actually a measure of the soap-consuming power of the water.

Total Hardness by Calculation.—Determine the amounts of CaO, MgO, and other metals and express results as parts per 100,000. Then Total Hardness as $CaCO_3 = 1.785\ CaO + 2.482\ MgO + 1.880\ Fe_2O_3{}^* + 2.945\ Al_2O_3$.

Total Hardness by Soap Method.—REAGENTS.—(1) *Standard $CaCl_2$ Solution.*—Dissolve 0.2 gram of pure calcite ($CaCO_3$) in a little dil. HCl, being careful to avoid loss of solution by spattering. Evaporate to dryness several times with distilled water to expel excess of acid, dissolve in distilled water and make up to 1 liter. 1 cc. = 0.0002 gram $CaCO_3$.

(2) *Standard Soap Solution.*—Dissolve 100 grams of dry white castile soap in 1 liter of 80% alcohol† and let stand several days before standardizing. Label this "stock soap solution." From the above stock solution dilute with 70% alcohol such a quantity that the resulting diluted soap solution will give a permanent lather when 6.40 cc. of it are properly added to 20 cc. of standard $CaCl_2$ solution. Usually 75–100 cc. of the stock soap solution are required for making 1 liter of the standard soap solution. Pure potassium oleate, made from lead plaster and K_2CO_3, may be used to advantage in place of castile soap.

STANDARDIZATION.—Pipette 20 cc. of the $CaCl_2$ solution into a 250-cc. glass-stoppered bottle and dilute to 50 cc. with distilled water which has been recently boiled and cooled. Then add from a burette 0.2–0.3 cc. of soap solution at a time, shaking the bottle vigorously after each addition, until a lather remains unbroken for 5 minutes over the entire surface of the water while the bottle lies upon its side. When the soap solution is of the strength above stated, then the quantity of $CaCO_3$ equivalent to each cc. of the soap solution is indicated in the following table:

* Or 2.688 Fe.

† Specially denatured alcohol formula No. 30 or pure methyl alcohol may be used in place of grain alcohol. Ordinary denatured alcohol, however, cannot be used because it does not give a clear solution when mixed with water.

TABLE XXVIII—HARDNESS IN PARTS OF $CaCO_3$ PER 100,000 FOR EACH 0.1 CC. OF SOAP SOLUTION WHEN 50 CC. OF WATER ARE TITRATED

Soap Solution, cc.	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0.0	....	....	....	....	....	....	....	0.0	0.16	0.32
1.0	0.48	0.63	0.79	0.95	1.11	1.27	1.43	1.56	1.69	1.82
2.0	1.95	2.08	2.21	2.34	2.47	2.60	2.73	2.86	2.99	3.12
3.0	3.25	3.38	3.51	3.64	3.77	3.80	4.03	4.16	4.29	4.43
4.0	4.57	4.71	4.86	5.00	5.14	5.29	5.43	5.57	5.71	5.86
5.0	6.00	6.14	6.29	6.43	6.57	6.71	6.86	7.00	7.14	7.29
6.0	7.43	7.57	7.71	7.86	8.00	8.14	8.29	8.43	8.57	8.71
7.0	8.86	9.00	9.14	9.29	9.43	9.57	9.71	9.86	10.00	10.15

PROCEDURE.—Measure 50 cc. of the water into a 250-cc. bottle and add soap solution in small quantities and in precisely the same manner as described under the standardization of the soap solution. From the result obtained, calculate from Table XXVIII the total hardness of the water, expressed as parts of $CaCO_3$ per 100,000.

When adding the soap solution to waters containing Mg salts, it is necessary to avoid mistaking the false or magnesium end-point for the true one. Consequently, after the titration is apparently finished, read the burette and add about 0.5 cc. more of soap solution. If the end-point was due to Mg, the lather will disappear. Soap solution must then be added until the true end-point is reached. Usually the false lather persists for less than 5 minutes.

When more than 7 cc. of soap solution are required for 50 cc. of the water, take less of the sample and dilute to 50 cc. with distilled water which has been recently boiled and cooled. This step reduces somewhat the disturbing influence of Mg salts, which consume more soap than equivalent weights of Ca salts. At best the soap method is not a precise test on account of the varying amounts of Ca and Mg present in different waters. For hard waters, especially in connection with processes for puri-

fication and softening, it is advisable not to use this method but to calculate the total hardness as previously described.

NOTES.—(1) When free CO_2 is present in the sample in considerable amount, it should be removed by aëration.

(2) The strength of the soap solution should be determined from time to time, to make sure that it has not materially changed while standing. Unless otherwise stated, record all results in terms of $CaCO_3$.

(3) English degrees of hardness, Clark's scale, are equivalent to grains of $CaCO_3$ per imperial gallon, and are multiplied by 1.43 to give parts per 100,000.

(4) French degrees of hardness represent parts of $CaCO_3$ per 100,000, and are the same as obtained by the above table.

(5) German degrees of hardness represent parts of CaO per 100,000 and are multiplied by 1.78 to give parts of $CaCO_3$ per 100,000.

IRON

General.—Iron in ground waters is usually in the soluble ferrous state, sometimes as carbonate or sulfate and also combined as organic matter. Ferric iron is seldom found in solution in appreciable quantities except in acid waters. Insoluble or colloidal iron is likely to be all ferric. Total Fe is determined in unfiltered samples; dissolved Fe, after filtration; the difference being suspended Fe. Ferrous Fe may be determined in filtered and unfiltered samples. Ferric Fe is the difference between the total and the ferrous.

Total Iron.—REAGENTS.—(1) *Standard Fe Solution.*—Dissolve 0.70 gram of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in 50 cc. of distilled water and add 20 cc. of dil. H_2SO_4. Warm slightly and add $KMnO_4$, little by little, until the Fe is completely oxidized. Dilute to 1 liter. 1 cc. = 0.0001 gram Fe.

(2) *KSCN or NH_4SCN Solution.*—Dissolve 20 grams in water and dilute to 1 liter.

(3) *Dilute HCl.*—Add to conc. HCl (free from HNO_3) an equal volume of distilled water. The solution is approximately 6 N.

(4) *0.2 N $KMnO_4$.*—Dissolve 6.30 grams in distilled water and dilute to a liter.

(5) *Conc. HCl.*—Free from iron.

PROCEDURE.—Evaporate 100 cc. (or less, if much Fe is present) of the sample to dryness. Use the residue from the Total Solids determination, if convenient. With silt-bearing waters the amount of Fe is sometimes so great that only 10 cc. of the sample

should be used. With such waters evaporate in the presence of 5–10 cc. of conc. HCl. If the sample contains much organic matter, destroy this by *gentle* ignition, taking care not to prolong the heating so as to make the Fe too difficultly soluble. Cool the dry residue and thoroughly moisten the whole inner surface of the dish with 5 cc. of dil. HCl (1:1). Warm for 2 or 3 minutes, swirling the dish gently to bring the hot acid in contact with all the residue. Warm 3 minutes longer with 5–10 cc. of hot distilled water and rinse the hot solution into a Nessler tube, filtering if necessary. Add a drop or two of $KMnO_4$ solution. If the pink color does not last for at least 5 minutes, add more, drop by drop.

Cool the oxidized solution and dilute to the mark. Have the Fe standards ready (see below) and add 5 cc. of the KSCN solution to the sample and each of the standards and compare immediately. With permanent standards the comparison must immediately follow the addition of the KSCN.

NOTE.—Directions should be followed exactly, since the color is deepened by an excess of KSCN, is diminished by excess of acid, and fades quickly on standing.

PREPARATION OF IRON STANDARDS.—Place in matched Nessler tubes measured volumes (0.5 to 4 cc.) of standard Fe solution covering the range of standards required for the sample, dilute to about 40 cc., add 5 cc. of dil. HCl (1:1) and 1–2 drops of $KMnO_4$ solution to each tube and dilute each to the mark. To each of these tubes, including the sample, add 5 cc. of KSCN solution, mix and compare immediately the colors developed. These standards are not permanent.

PREPARATION OF PERMANENT STANDARDS.—The permanent standards are prepared from the following solutions:

(*a*) K_2PtCl_6.—Dissolve 2 grams in distilled water, add 100 cc. of conc. HCl and dilute to 1 liter.

(*b*) $CoCl_2 \cdot 6H_2O$.—Dissolve 24 grams of the dry crystals in a small volume of distilled water, add 100 cc. of conc. HCl and dilute to 1 liter.

Place in 50-cc. Nessler tubes the volumes of platinum and cobalt solutions specified in Table XXIX, and make up to 50 cc. with distilled water. The Fe equivalent of these standards is shown in the first column.

TABLE XXIX—PERMANENT STANDARDS FOR Fe DETERMINATION

Iron, *gram*	Pt Solution, *cc.*	Co Solution, *cc.*
0.00000	0	0
0.00001	2	1
0.00003	6	3
0.00005	10	5
0.00007	14	7.5
0.00010	20	11
0.00015	28	17

Ferrous Iron.—REAGENTS.—(1) *Potassium Ferricyanide.*—Dissolve 0.5 gram of fresh crystals in a small amount of water and dilute to 100 cc. This solution must be freshly prepared.

(2) *Dilute H_2SO_4.*—Mix 1 volume of conc. H_2SO_4, free from Fe, with 5 volumes of distilled water.

(3) *Standard Ferrous Solution.*—Dissolve 0.70 gram of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in a large volume of freshly boiled, distilled water to which 10 cc. of the dil. H_2SO_4 have been added, and dilute to 1 liter. This solution must be freshly prepared. 1 cc. = 0.0001 gram Fe.

PROCEDURE.—Add 10 cc. of the dil. H_2SO_4 to 50 cc. of the sample, remove suspended matter by filtration if necessary, and add 15 cc. of $K_3Fe(CN)_6$ solution. Dilute to the mark in a 100-cc. Nessler tube with distilled water that has been freshly boiled and cooled. Compare the color developed in the sample with that in standards made at the same time from the standard ferrous solution as follows: Place in 100-cc. Nessler tubes, in the following order, 75 cc. of distilled water, 10 cc. of dil. H_2SO_4 and 15 cc. of $K_3Fe(CN)_6$ solution, and mix each tube thoroughly. Add various volumes of the standard ferrous solution to several tubes, mix well and compare immediately the resulting colors with that of the sample.

REFERENCE.—American Public Health Association: "Standard Methods of Water Analysis," 6th ed. (1925)

INDUSTRIAL WATER

General.—This method applies to the mineral analysis of waters to be used for boilers and for general manufacturing pur-

poses.* It is fully realized that it is open to criticism from a strictly chemical standpoint (*e.g.*, it takes no account of the possible presence of potassium salts or bicarbonates) but the results give the desired information for practically all technical purposes.

The quantity of water which must be taken for analysis depends upon the amount of dissolved solids which it contains. As a general rule, about 1 liter is a suitable amount of water for evaporation. One U. S. gallon of pure water at 60° F. contains 58,334.9 grains. If, therefore, 583.3 cc. of water are taken for analysis, the weight in centigrams of the various substances found will give directly the number of grains per U. S. gallon. For ordinary waters, therefore, evaporate 1167 cc. and divide by 2 the number of centigrams obtained. The results will be grains per gallon.

It is convenient to have several flasks specially calibrated to contain 1167 cc., 583.3 cc., 291.7 cc. and 116.7 cc., respectively. These may be prepared by selecting ordinary volumetric flasks of 1000 cc., 500 cc., 250 cc. and 100 cc., respectively, choosing flasks where the graduation mark is low on the neck. Weigh each flask, place in it the proper number of grams of water at 20° C. and make a new mark at the meniscus of the water; or, fill each to its original mark, add the proper number of cc. of water from a burette to bring the volume to the proper figure, and make the new mark, preferably by etching. A suitable flask for the largest size is the kind with a bulb in the neck and 2 graduations at 1000 and 1100 cc.

If 1000 cc. are taken for analysis, multiply the number of centigrams found by 0.5833 to obtain grains per gallon.

Free Carbon Dioxide.—Because of the ease with which free CO_2 escapes from water, particularly when the gas is present in large amounts, a special sample should be collected for this determination, which should preferably be made at the time of collection. If the analysis cannot be made at the time of collection, approximate results with water not too high in free CO_2 can be obtained on samples collected in bottles completely filled so as to leave no air space under the stopper. Bottled samples should be kept, until tested, at a temperature lower than that

* For the determination of dissolved oxygen see page 703.

of the water when collected. If mineral acids or certain salts are present correction must be made.* At best the results of the titration are uncertain because the proper end-point for correct results differs in color with different types of water.

To 291.7 cc. of the sample (measured in a specially graduated flask) contained in a 400-cc. Erlenmeyer flask add 1 cc. of phenolphthalein indicator solution, and titrate rapidly with 0.01 N Na_2CO_3 till a faint pink color persists after gentle stirring. Take care not to breathe into the flask and do not use a flask unnecessarily large. Calculate the titration to CO_2, according to the reaction:

$$Na_2CO_3+CO_2+H_2O=2NaHCO_3.$$

CALCULATION.—1 cc. 0.01 N $Na_2CO_3=0.00022$ gram CO_2.

Multiply by 2 the number of centigrams of CO_2 obtained and the result (in the absence of free mineral acids or acid salts) will be grains per U. S. gallon.

NOTE.—If the sample contains over 46 grains of $NaHCO_3$ per gallon or if the total carbonate hardness is over 10 (corresponding to the equivalent of 5.8 grains of $CaCO_3$ per gallon) it must be diluted with CO_2-free water before titration, to prevent the precipitation of $CaCO_3$ and $MgCO_3$ with consequent liberation of CO_2.

Suspended Matter.—If the sample is decidedly turbid or contains an appreciable amount of suspended matter, shake thoroughly and measure out 1167 cc. in a specially graduated flask. Filter through a filter paper† which has previously been dried at 105° C. and weighed in a weighing bottle, collecting the clear filtrate in a clean beaker or flask. Wash the residue on the filter paper once with distilled water and dry at 105° C. in the same weighing bottle. Cool in a desiccator and weigh. Divide by 2 the number of centigrams to obtain the grains of total suspended matter per gallon.

Ignite the filter paper in a weighed platinum crucible, dry in a desiccator and weigh. This weight will give the amount of nonvolatile suspended matter.

* See under Carbonic Acid (p. 712) and Acidity (p. 713).

† A Gooch crucible may be used if preferred, although, if the water contains much organic matter or fine silt, these may have a tendency to clog the asbestos mat

Total Solids.—Evaporate the filtrate obtained above in a weighed platinum dish on the steam bath. Finally dry to constant weight in the oven at 105° C. Usually 0.5–1 hour is sufficient unless the amount of solids is unusually high. With highly mineralized waters it is advisable to dry at 180° C. Cool in a desiccator and weigh.

NOTE.—The evaporation may be hurried by gentle boiling on a hot plate or over a free flame on an asbestos mat, taking care not to lose any by spattering and not to let it go to dryness before transferring to the steam bath. In urgent cases clamp a horizontal glass tube about 0.5 inch above the top of the dish, with the open end at about the center, and connect the other end to suction or a gentle air blast to remove the vapors.

Organic and Volatile Matter.—Manipulate the dish in a Tirrill flame with a pair of tongs until the organic matter is burned off at as low a temperature as possible. Cool in a desiccator and weigh. Report the loss as Organic and Volatile Matter.

NOTE.—This result will generally be too high, due to loss of CO_2 from carbonates, and is used only as a rough check on the analysis, the actual organic and volatile matter in the final calculation being taken "by difference."

Total Mineral Matter as Sulfates.—Add a few drops of dil. H_2SO_4 to the above residue in the platinum dish (note here whether there is an effervescence of carbonates). Manipulate the dish so that the acid will come in contact with all of the residue. If there is a strong effervescence, it will be advisable to add a few more drops of the acid.

Evaporate to dryness on the steam bath and then to fumes of SO_3 on the hot plate. (If no white fumes are obtained, insufficient H_2SO_4 has been added.) Finish the heating carefully over a free flame until the evolution of SO_3 fumes ceases. Then heat for some time at a red heat to decompose any $FeSO_4$ into Fe_2O_3. Cool in a desiccator and weigh. The combined weight represents the mineral matter as Fe_2O_3, SiO_2, Al_2O_3, $CaSO_4$, $MgSO_4$ and alkaline sulfates. For all ordinary purposes the latter may be considered Na_2SO_4.

Silica.—Add a few cc. of conc. HCl to the above residue and warm until all the Fe_2O_3 dissolves. Dilute with about twice the volume of water and continue the heating for a short time. During the heating loosen the insoluble matter adhering to the dish

with a rubber policeman and stir to hasten the solution. Filter through a small ashless filter and wash the residue with hot water. Place the filter paper containing the insoluble matter in the original platinum dish and burn off the paper, taking care to protect the dish from drafts of air. Ignite strongly, cool in a desiccator, and weigh as SiO_2.

NOTE.—If the water is to be used for boiler purposes, it is not necessary to determine the silica separately unless a large amount is present.

Iron Oxide and Alumina.—Heat the filtrate from the SiO_2 (or, in case the SiO_2 is not to be determined separately, the unfiltered solution of the sulfates) nearly to boiling. Add a slight excess of NH_4OH and digest on the steam bath until the odor of NH_3 is nearly gone. Filter through a small filter. Ignite strongly in a platinum crucible, cool in a desiccator and weigh as $Fe_2O_3+Al_2O_3(+SiO_2)$.

NOTE.—If Mn is suspected to be present, add 5 cc. of strong Br water and boil before adding the NH_4OH to precipitate Fe and Al. In this case the Mn will come down with the Fe and Al after treatment with Br water and NH_4OH, and if it is desired to know the amount, it must be determined in a separate portion of the water and the amount (calculated as Mn_3O_4) subtracted from the total weight of the NH_4OH precipitate (see pp. 136 and 185, under Manganese).

Iron Oxide.—If it is desired to determine the Fe_2O_3 separately, fuse the residue in the crucible with a little $KHSO_4$. Dissolve the fusion in water and determine the Fe_2O_3 colorimetrically with KSCN, matching the color against a standard Fe solution (see under Total Iron on page 691).

Alumina.—Ordinarily Al_2O_3 is not determined separately. If, however, the colorimetric determination of Fe leaves considerable to be accounted for in the NH_4OH precipitate, the difference may be considered as Al_2O_3.

Lime.—Heat to boiling the filtrate from the NH_4OH precipitate. Add 5 cc. of $(NH_4)_2C_2O_4$ reagent solution and digest on the steam bath until the precipitate has settled. Filter through a small ashless filter, wash well with hot water, ignite thoroughly in a platinum crucible and weigh as CaO.

NOTE.—Instead of igniting the CaC_2O_4 it may be titrated with 0.1 N $KMnO_4$ as follows:

In a 400-cc. beaker place about 125 cc. of distilled water and add 5–7 cc. of conc. H_2SO_4. Drop the moist filter paper containing the CaC_2O_4 into this and heat to about 70° C. Stir to effect the decomposition of the CaC_2O_4 but avoid excessive disintegration of the paper. Titrate the hot solution, with constant stirring, with 0.1 N or 0.01 N $KMnO_4$ until a permanent pink color forms.

CALCULATION.—1 cc. 0.1 N $KMnO_4 = 0.002804$ gram CaO.

Magnesia.—Make the filtrate from the CaO determination slightly acid with HCl and evaporate until crystallization starts. Dissolve any crystals formed with a small amount of distilled water. Cool, and add 25 cc. of a 10% solution of $(NH_4)_2HPO_4$. (It is permissible to use Na_2HPO_4 or $NaNH_4HPO_4$.) Then add slowly with constant stirring conc. NH_4OH until neutral, finally adding about 2 cc. in excess. This is best done from a burette or a Mohr pipette. Let stand overnight, if possible, or cool in ice water and stir for ½ hour. Filter through a weighed Gooch crucible and wash with magnesia wash solution.* Dry the precipitate and then finally ignite strongly, cool and weigh as $Mg_2P_2O_7$. Calculate to MgO.

CALCULATION.—$Mg_2P_2O_7 \times 0.3621 = MgO$.

Alkalies.—For all ordinary purposes the alkalies may be regarded as consisting wholly of Na_2O and are obtained by calculation as described under Calculation of Results.

Sulfur Trioxide.—To 291.7 cc. of the sample (measured in a specially graduated flask), contained in a 400-cc. beaker, add 5 cc. of dil. HCl. Heat to boiling and then add, drop by drop, 5 cc. of 10% $BaCl_2$ solution. Let stand overnight, protected from SO_3 fumes. Filter, wash with hot water, ignite the precipitate and weigh as $BaSO_4$. Calculate to SO_3 and multiply the number of centigrams of SO_3 by 2 to obtain grains per gallon.

CALCULATION.—$BaSO_4 \times 0.3430 = SO_3$.

Chlorine.—Determine Cl by the procedure given on page 686. If 116.7 cc. of the water are used, then the number of cc. of the standard $AgNO_3$ solution, divided by 4, will give directly grains of Cl per U. S. gallon.

If the water contains over 60 grains of Cl, make the determination gravimetrically, weighing the AgCl.

* Magnesia wash solution: Add 200 grams of NH_4NO_3 to 400 cc. of conc. NH_4OH; mix and dilute with water to 1 liter.

Calculation of Results.—Calculate the CaO and MgO to $CaSO_4$ and $MgSO_4$, respectively. Add to the sum of these the amount of Fe_2O_3, SiO_2 and Al_2O_3 and subtract this sum from the total weight of mineral matter calculated as sulfates, as previously determined. Consider the difference as Na_2SO_4 and calculate the equivalent amount of Na_2O.

Calculate the total Cl to NaCl, if there is enough Na_2O to combine with it. If, however, there is an excess of Cl over the Na_2O, calculate the remainder to $MgCl_2$. If the Na_2O is in excess of the Cl, calculate the excess to Na_2SO_4 and then the remainder, if any, to Na_2CO_3. If there is insufficient Na_2O left from the NaCl calculation to combine with all the SO_3, calculate the excess of the latter to $CaSO_4$. If the SO_3 is still in excess, combine it with any MgO not satisfied with Cl, and if there is still an excess, calculate it to H_2SO_4. (In this case, of course, the water would show an acid reaction to methyl orange and litmus.) Calculate any MgO or CaO not accounted for by Cl and SO_3 to $CaCO_3$ and $MgCO_3$, respectively. If the Na_2O is in excess of both Cl and SO_3, calculate the excess to Na_2CO_3. The Fe_2O_3 is probably present as $FeSO_4$ or $FeCO_3$ but for practical purposes this calculation is unnecessary. The SiO_2 is usually reported as such, although in water containing a considerable amount, and also containing Na_2CO_3,* it may be present as sodium silicate.

Report the final results as follows:

	Grains per U. S. gallon
Free carbon dioxide (CO_2)	
Suspended matter:	
Organic and volatile	
Non-volatile	
Total	
On Filtered Sample	
Silica (SiO_2)	
Alumina (Al_2O_3)	
Iron oxide (Fe_2O_3)	
Lime (CaO)	
Magnesia (MgO)	

* Water containing Na_2CO_3 will be alkaline to phenolphthalein, although, even if the water is neutral to this indicator, it may still contain $NaHCO_3$, in which case it will be alkaline to methyl orange.

	Grains per U. S. gallon
Sodium oxide (Na_2O)	
Sulfur trioxide (SO_3)	
Chlorine (Cl)	
Probably combined as follows:	
Silica (SiO_2)	
Iron oxide (Fe_2O_3)	
Alumina (Al_2O_3)	
Sodium chloride (NaCl)	
Sodium sulfate (Na_2SO_4)	
Sodium carbonate (Na_2CO_3)	
Magnesium chloride ($MgCl_2$)	
Magnesium sulfate ($MgSO_4$)	
Magnesium carbonate ($MgCO_3$)	
Calcium chloride ($CaCl_2$)	
Calcium sulfate ($CaSO_4$)	
Calcium carbonate ($CaCO_3$)	
Organic and volatile matter	
Residue on evaporation	

NOTES.—(1) In waters which are to be used for boiler purposes it is sufficient ordinarily to report Fe_2O_3, Al_2O_3 and SiO_2 together, and not separately.

(2) The following are incrusting or scale-forming solids:

Silica.
Oxides of iron and aluminum.
Calcium sulfate and carbonate.
Calcium chloride (corrosive).
Magnesium sulfate (forms scale only in the presence of $CaCO_3$).
Magnesium chloride (strongly corrosive).
Magnesium carbonate.

The following are non-incrusting solids:

Chlorides, sulfates, and carbonates of the alkalies.
Organic matter.

(3) The general grading of waters for boiler purposes, according to the contents of scale-forming matter, is as follows:

Less than 10 grains per gallon	Good
10–20 grains	Fair
20–30 grains	Poor
30–40 grains	Bad
Over 40 grains	Very bad

(4) Grains per gallon $\times \frac{10}{7}$ = pounds per 10,000 gallons.

Factors.—The following factors will be found useful in calculating results:

Given	Wanted	Factor	Log
$CaCl_2$	CaO	0.5052	9.70346
CaO	$CaCO_3$	1.7847	0.25157
	$CaSO_4$	2.4279	0.38523
$CaSO_4$	CaO	0.4119	9.61479
Cl	$CaCl_2$	1.5650	0.19451
	KCl	2.1026	0.32276
	$MgCl_2$	1.3429	0.12805
	NaCl	1.6486	0.21712
CO_2	Na_2CO_3	2.4090	0.38184
Fe_2O_3	$FeCO_3$	1.4509	0.16164
KCl	K_2O	0.6317	9.80050
	K_2SO_4	1.1686	0.06766
K_2O	K_2CO_3	1.4671	0.16647
	K_2SO_4	1.8500	0.26717
$MgCl_2$	MgO	0.4234	9.62675
MgO	$CaCO_3$	2.4819	0.39478
	$MgCO_3$	2.0915	0.32046
	$MgSO_4$	2.9857	0.47504
$MgSO_4$	MgO	0.3349	9.52492
Mn_3O_4	$MnCO_3$	1.5070	0.17811
NaCl	Cl	0.6066	9.78290
	Na_2O	0.5303	9.72452
Na_2CO_3	Na_2SO_4	1.3402	0.12717
Na_2O	NaCl	1.8858	0.27550
	Na_2CO_3	1.7098	0.23295
	Na_2SiO_3	1.9687	0.29418
	Na_2SO_4	2.2914	0.36010
Na_2SO_4	Na_2CO_3	0.7462	9.87286
	Na_2O	0.4364	9.63989
	SO_3	0.5636	9.75097

Given	Wanted	Factor	Log
Na_2SiO_3	Na_2O	0.5079	9.70578
SiO_2	CO_2	0.7326	9.86487
	NaS_2iO_3	2.0321	0.30794
SO_3	$CaSO_4$	1.7004	0.23055
	$MgSO_4$	1.5036	0.17712
	Na_2SO_4	1.7743	0.24903
	H_2SO_4	1.2250	0.08814

REFERENCES.—LOW: "Technical Methods of Ore Analysis;" Tillman and Henblein, *Z. Nahr.-Genussm.*, **24,** 429; *C. A.*, **7,** 38.

OIL IN BOILER-FEED WATERS

It is often important to determine the amount of oil in a boiler-feed water, as it is generally considered dangerous to allow more oil in the water than 0.5 grain per U. S. gallon. Samples of water which are to be tested for oil should be collected in gallon glass-stoppered containers, clean and absolutely free from oil.

Upon receipt of the sample, weigh it in the bottle. Transfer the entire sample to a large separatory funnel, which is clean and entirely free from oil, and shake out with about 50 cc. of redistilled chloroform. In case the separatory funnel is not large enough to hold all the sample, 2 funnels may be used; in which case draw off into the second funnel the $CHCl_3$ used in shaking out the water in the first funnel, then add more of the water to the second funnel from the original container and shake out with the same $CHCl_3$. After the container has been emptied of the water, add to it about 50 cc. of $CHCl_3$, replace the stopper and shake thoroughly to dissolve any oil which may stick to the sides of the bottle or the stopper. Pour this $CHCl_3$ into the separatory funnel containing the remainder of the $CHCl_3$ and draw the combined extracts off carefully. If the latter is clear and free from water, evaporate it in a weighed flask and dry to constant weight at 100° C. In case the extract is not clear, filter it before evaporating and wash the filter with a fresh portion of $CHCl_3$.

Dry the original container with a blast of air and weigh it. Calculate the total volume of the sample, considering 1 gram equivalent to 1 cc. Calculate the weight of oil obtained to grains per U. S. gallon of the water.

$$\text{Calculation.}—\frac{\text{Wt. of oil (grams)}}{\text{cc. of sample}} \times 58{,}300 = \text{grains per gallon.}$$

DISSOLVED OXYGEN IN WATER

General.—Determine dissolved oxygen by the Rideal Stewart modification of the Winkler method on all waters containing 0.01 part per 100,000 or more of nitrite N. On other waters the original Winkler method may be used. The procedure given below is the Rideal Stewart modification. For the unmodified Winkler procedure omit the first 3 steps, following the procedure from the addition of $MnSO_4$, except that the volume of the alkaline KI added should be reduced to 1 cc.

Collection of Sample.—Collect the sample in a narrow glass-stoppered bottle of 250–270-cc. capacity. Employ the following procedure in order to avoid entrainment or absorption of atmospheric oxygen. In collecting from a tap fill the bottle through a glass or rubber tube extending well into the tap and to the bottom of the bottle. To avoid air bubbles let the bottle overflow for several minutes, and then carefully replace the glass stopper so that no air bubble is entrained. In collecting from the surface of a pond or tank connect the sample bottle to a bottle of 1-liter capacity. Provide each bottle with a 2-hole rubber stopper having one glass tube extending to the bottom and another glass tube entering but not projecting into the bottle. Connect the short tube of the sample bottle with the long tube of the liter bottle. Immerse the sample bottle in the water and apply suction to the outlet of the liter bottle. To collect a sample at any depth arrange the two bottles so that the outlet tube of the liter bottle is at a higher elevation than the inlet tube of the sample bottle. Lower the two bottles, in any convenient form of cage properly weighted, to the desired depth. Water entering during the descent will be flushed through into the liter bottle. When air bubbles cease rising to the surface, raise the bottles. Finally replace the perforated stopper in such a manner as to avoid entraining bubbles of air.

Reagents.—(1) *Conc.* H_2SO_4.

(2) *$KMnO_4$ Solution.*—6.32 grams per liter.

(3) *$K_2C_2O_4 \cdot H_2O$ Solution.*—20 grams per liter.

(4) *$MnSO_4 \cdot 4H_2O$.*—480 grams per liter.

(5) *Alkaline KI Solution.*—Dissolve 700 grams of KOH (or 500 grams of NaOH) and 150 grams of KI in water and dilute to 1 liter.

(6) *0.025 N Sodium Thiosulfate.*—Dissolve 6.205 grams of pure recrystallized $Na_2S_2O_3 \cdot 5H_2O$ in water and dilute to 1 liter with freshly boiled and cooled distilled water. Each cc. is equivalent to 0.0002 gram of oxygen, or 0.1395 cc. of oxygen at 0° C. and 760-mm. pressure. Since this solution is not permanent, it should be standardized occasionally against a 0.025 N solution of $K_2Cr_2O_7$ (see page 10).

(7) *Starch Solution.*—Mix a small amount of clean starch with cold water to form a thin paste and stir the mixture into 150–200 times its weight of water. Boil for a few minutes and sterilize. Preserve by adding a few drops of $CHCl_3$.

Procedure.—Remove the stopper from the bottle containing the sample and add first 0.7 cc. of the conc. H_2SO_4, and then 1 cc. of the $KMnO_4$ solution. These and all other reagents should be introduced by pipette under the surface of the liquid. Insert the stopper and mix by inverting the bottle several times. If a noticeable excess of $KMnO_4$ is not present after 20 minutes, again add 1 cc. of the $KMnO_4$ solution; if this is still insufficient, use a stronger $KMnO_4$ solution. After 20 minutes have elapsed destroy the excess of $KMnO_4$ by adding 1 cc. of $K_2C_2O_4$ solution, restopper the bottle at once and mix its contents. Add 1 cc. of the $MnSO_4$ solution and 3 cc. of the alkaline KI solution. Allow the precipitate to settle. Add 1 cc. of the conc. H_2SO_4 and mix by shaking.

The procedure to this point must be carried out in the field, but after the acid has been added and the stopper replaced there is no further change, and the rest of the test may be performed within a few hours, as convenient. Transfer 200 cc. of the contents of the bottle to a flask and titrate with 0.025 N $Na_2S_2O_3$, using a few cc. of the starch solution as indicator toward the end of the titration. Do not add the starch solution until the color has become faint yellow. Titrate until the blue color disappears.

Calculation of Results.—Report the oxygen in parts per million by weight. It is sometimes convenient to know the number of cc. per liter of the gas at 0° C. temperature and 760-mm. pressure and also to know the percentage which the amount of gas present is of the maximum amount capable of being dissolved by distilled water at the same temperature and pressure. If 200 cc. of the sample are taken, the number of cc. of 0.025 N thiosulfate used is equal to parts of oxygen per million. Corrections for volume of reagents added amount to less than 3% and are not justified except in work of unusual precision.

To obtain the result in cc. per liter multiply parts per million by 0.698. To obtain the result in percentage of saturation divide the number of parts per million by the figure in Table XXX opposite the temperature of the water and under the proper chloride figure, and multiply by 100. The last column of the table permits interpolation for intermediate chlorine values. At elevations differing considerably from mean sea level and for accurate work, attention must be given to barometric pressure, the normal pressure in the region being preferable to the specific pressure at the time of sampling. The term "saturation" refers to a condition of equilibrium between the solution and an oxygen pressure in the atmosphere corresponding to 158.8 mm. or approximately $\frac{1}{5}$ atmosphere. The true saturation or equilibrium between the solution and pure oxygen is nearly 5 times this value, and consequently values in excess of 100% saturation frequently occur in the presence of oxygen-forming plants.

Reference.—American Public Health Association: "Standard Methods of Water Analysis" (1925).

BOILER SCALE

General.—Break up pieces as representative as possible of the scale and grind in an iron or porcelain mortar. Then quarter down and pulverize a small sample finely in an agate mortar for analysis.

Moisture.—Dry 5 grams of the powder at 105° C. to constant weight. Report the loss in weight as Moisture.

Oil.—Transfer the dry powder left from the moisture determination to an extraction thimble and extract with ether in a

TABLE XXX—SOLUBILITY OF O_2 IN FRESH AND SALINE WATERS AT VARIOUS TEMPERATURES WHEN EXPOSED TO AN ATMOSPHERE CONTAINING 20.9% OF O_2 UNDER A PRESSURE OF 760 MM.*

Temperature	Cl in Water (Parts per 100,000)					Difference per 10 Parts of Cl per 100,000
	0	500	1000	1500	2000	
° C.	*Dissolved O_2 in Parts per Million*					*Parts per Million*
0	14.62	13.79	12.97	12.14	11.32	0.0165
1	14.23	13.41	12.61	11.82	11.03	0.0160
2	13.84	13.05	12.28	11.52	10.76	0.0154
3	13.48	12.72	11.98	11.24	10.50	0.0149
4	13.13	12.41	11.69	10.97	10.25	0.0144
5	12.80	12.09	11.39	10.70	10.01	0.0140
6	12.48	11.79	11.12	10.45	9.78	0.0135
7	12.17	11.51	10.85	10.21	9.57	0.0130
8	11.87	11.24	10.61	9.98	9.36	0.0125
9	11.59	10.97	10.36	9.76	9.17	0.0121
10	11.33	10.73	10.13	9.55	8.98	0.0118
11	11.08	10.49	9.92	9.35	8.80	0.0114
12	10.83	10.28	9.72	9.17	8.62	0.0110
13	10.60	10.05	9.52	8.98	8.46	0.0107
14	10.37	9.85	9.32	8.80	8.30	0.0104
15	10.15	9.65	9.14	8.63	8.14	0.0100
16	9.95	9.46	8.96	8.47	7.99	0.0098
17	9.74	9.26	8.78	8.30	7.84	0.0095
18	9.54	9.07	8.62	8.15	7.70	0.0092
19	9.35	8.89	8.45	8.00	7.56	0.0089
20	9.17	8.73	8.30	7.86	7.42	0.0088
21	8.99	8.57	8.14	7.71	7.28	0.0086
22	8.83	8.42	7.99	7.57	7.14	0.0084
23	8.68	8.27	7.85	7.43	7.00	0.0083
24	8.53	8.12	7.71	7.30	6.87	0.0083
25	8.38	7.96	7.56	7.15	6.74	0.0082
26	8.22	7.81	7.42	7.02	6.61	0.0080
27	8.07	7.67	7.28	6.88	6.49	0.0079
28	7.92	7.53	7.14	6.75	6.37	0.0078
29	7.77	7.39	7.00	6.62	6.25	0.0076
30	7.63	7.25	6.86	6.49	6.13	0.0075

*American Public Health Association: "Standard Methods for the Examination of Water and Sewage," 6th ed., 62 (1925). (For solubilities at other pressures multiply the above figures by $\frac{B}{760}$, where B = barometic pressure in mm.)

Soxhlet extractor in the usual way, collecting the extract in a weighed Soxhlet flask. Distill off the ether and dry the flask at 100° C. to constant weight.

Organic and Volatile Matter.—Weigh out 1 gram of the powdered material in a platinum crucible and gently ignite until the organic matter is burned off. Cool the crucible in a desiccator and weigh. From this weight subtract the moisture previously determined and report the difference as Organic and Volatile Matter (see note 2).

Silicious Matter.—Transfer the residue from the above determination with a little water to a 250-cc. beaker. Cover the beaker with a watch glass and add HCl in slight excess. Dilute to about 150 cc., heat to boiling for a few minutes and filter. Wash thoroughly with hot water. Ignite the residue in a platinum crucible, first over a burner and then in a blast lamp. Cool in a desiccator and weigh.

Iron and Aluminum Oxides.—To the filtrate from the silicious matter add a few drops of conc. HNO_3 and heat to boiling. Add 10 cc. of 10% NH_4Cl solution and then NH_4OH in excess. Boil until there is only a faint odor of NH_3. Filter and wash thoroughly. Ignite, blast, cool and weigh as $Fe_2O_3+Al_2O_3$.

Lime.—To the filtrate from the above add a few cc. of NH_4OH, heat to boiling and add $(NH_4)_2C_2O_4$ solution in excess. Boil until the precipitate becomes granular. Let stand in a warm place until the solution becomes clear. Filter and wash with hot water. Ignite the precipitate first in a Tirrill burner and then in a blast lamp to constant weight. Cool in a desiccator and weigh rapidly as CaO. (If preferred the CaC_2O_4 may be titrated with 0.1 N $KMnO_4$ as on page 697.)

Magnesia.—Make the filtrate from the CaO determination slightly acid with HCl and evaporate until crystallization begins. Add sufficient water to just redissolve any crystals which form. Cool thoroughly. Add at least 10 cc. of 10% sodium phosphate or ammonium phosphate solution. Stir briskly with a stirring rod and rubber policeman until precipitation starts, and add about $\frac{1}{4}$ the volume of strong NH_4OH. Let stand overnight, if possible. If the analysis is urgent, place the beaker in ice water and stir for $\frac{1}{2}$ hour. Filter the precipitate on a weighed Gooch crucible and wash with magnesia wash water (see p. 698). Dry the

precipitate in the oven and ignite strongly over a Tirrill burner to constant weight as $Mg_2P_2O_7$. Calculate to MgO.

CALCULATION.—$Mg_2P_2O_7 \times 0.3621 = MgO$.

Sulfur Trioxide.—Boil 1 gram of the finely powdered material with conc. HCl, dilute with 2 volumes of water and boil again. Filter and wash thoroughly with hot water. Heat the filtrate to boiling and add very slowly 10 cc. of 10% $BaCl_2$ solution. Boil gently until the precipitate settles clear. Filter, wash free from chlorides with hot water, ignite the precipitate, and weigh as $BaSO_4$. Calculate to SO_3.

CALCULATION.—$BaSO_4 \times 0.3430 = SO_3$.

Chlorine.—Weigh out 5 grams of the dry powdered scale. Add 100 cc. of water and heat to boiling. Filter and wash thoroughly, catching the filtrate in a porcelain dish. Cool, add a few drops of K_2CrO_4 indicator and titrate with standard $AgNO_3$ solution to the appearance of a reddish color. Since the amount of chlorides present is generally small, a weak $AgNO_3$ solution (0.01 N) should be used in titrating. If the scale forms an alkaline solution, it must be exactly neutralized with dil. H_2SO_4 and phenolphthalein before titrating.

CALCULATION.—1 cc. 0.01 N $AgNO_3 = 0.000355$ gram Cl.

Final Calculations.—Calculate the Cl (if any is present) to NaCl. Calculate the SO_3 to $CaSO_4$; and if an excess of SO_3 remains, calculate it to $MgSO_4$. In case the SO_3 is insufficient to combine with the CaO, calculate the remainder of the CaO to $CaCO_3$. Report any MgO which is in excess of the SO_3 as MgO and not as $MgCO_3$, since the latter is decomposed at the temperature of the boiler.

NOTES.—(1) Other substances such as copper, zinc, etc., from local sources are occasionally found in boiler scales. If such are present, they may be determined by the usual quantitative methods.

(2) The determination of organic and volatile matter is usually too high, owing to the partial loss of CO_2 from carbonates, so it is generally advisable to take the organic and volatile "by difference"—merely using the actual determination as a rough check upon it. Any oil present is, of course, included in the organic and volatile matter.

(3) As extreme accuracy is not usually necessary in boiler scale analysis, a single precipitation of the CaC_2O_4 is sufficient. The possibility of the presense of $Ca_3(PO_4)_2$ should be considered, however, as some "boiler compounds" used for treating boiler water contain alkali phosphates.

(4) The following factors will be found useful:

$$CaO \times 1.785 = CaCO_3.$$
$$CaO \times 2.428 = CaSO_4.$$
$$CaSO_4 \times 0.412 = CaO.$$
$$Cl \times 1.65 = NaCl.$$
$$MgO \times 2.986 = MgSO_4.$$
$$SO_3 \times 1.700 = CaSO_4.$$
$$SO_3 \times 1.504 = MgSO_4.$$

MINERAL WATERS

General.—This method is for the analysis of mineral spring waters, such as those containing lithia, sulfur, etc., and for the determination of special mineral constituents of water such as Mn, I, Br, etc. For a complete mineral analysis of water the determinations in this method should be carried out in connection with the ordinary industrial and sanitary analyses (pp. 668 and 693) with such modifications as are below indicated.

Turbid waters should be filtered and the composition of the suspended matter separately determined, if desired, or otherwise merely reported as Suspended Matter. Report results in parts per 100,000 unless otherwise directed.

Alkalinity.—The alkalinity of natural waters ordinarily includes carbonates and bicarbonates of lime and magnesia. In some waters in the West it also includes Na_2CO_3 or K_2CO_3. Waters that have been softened may contain alkalinity due to $Ca(OH)_2$ (lime water) and also Na_2CO_3 (soda ash). Occasionally the alkalinity is due to borates, silicates, or phosphates.

Alkalinity is determined by titration with a standard solution of strong acid to certain standard hydrogen-ion concentrations, using indicators which show definite color changes at these points. Since dilute bicarbonate solutions have a hydrogen-ion concentration of about $1 \times 10^{-8.0}$(or pH 8.0) and dilute carbonic acid solutions a hydrogen-ion concentration of $1 \times 10^{-4.0}$ (or pH 4.0), indicators should be used which show definite color changes at these points. The amount of standard acid required to bring the water to pH 8 measures the hydroxides plus $\frac{1}{2}$ the normal carbonates, and phenolphthalein is a suitable indicator for this. The amount of acid required to bring it to pH 4 corresponds to the total alkalinity and for this methyl orange or erythrosine

may be used, the latter being preferable for waters containing sulfates of Fe or Al.

Alkalinity, unless otherwise indicated, is expressed in terms of $CaCO_3$ as parts per 100,000.

Phenolphthalein Alkalinity.—Add 4 drops of phenolphthalein indicator to 50 or 100 cc. of the sample in a white porcelain casserole or an Erlenmeyer flask over a white surface. If the solution becomes colored, hydroxide or normal carbonate is present. Add 0.02 N H_2SO_4 from a burette until the coloration disappears. The phenolphthalein alkalinity in parts of $CaCO_3$ per 100,000 is equal to the number of cc. of 0.02 N acid used on a 100-cc. sample.

Methyl Orange (Total) Alkalinity.—Add 2 drops of methyl orange indicator to 50 or 100 cc. of the sample, or to the solution to which phenolphthalein has been added, in a white porcelain casserole or an Erlenmeyer flask over a white surface. If the solution becomes yellow, hydroxide, normal carbonate, or bicarbonate is present. Add 0.02 N H_2SO_4 until the faintest pink color appears, *i.e.*, until the color of the solution is no longer pure yellow. The methyl orange alkalinity in parts of $CaCO_3$ per 100,000 is equivalent to the number of cc. of 0.02 N acid used for a 100-cc. sample.

Erythrosine (Total) Aklalinity.—Add 5 cc. of $CHCl_3$ (neutral to erythrosine) and 1 cc. of erythrosine indicator* to 50 or 100 cc. of the sample in a 250-cc. clear glass-stoppered bottle. If the $CHCl_3$ becomes rose colored on shaking, hydroxide, bicarbonate, or normal carbonate is present. Add 0.02 N H_2SO_4 until the $CHCl_3$ becomes colorless on shaking. A white surface behind the bottle facilitates detection of traces of color when the endpoint is approached. The calculation is the same as with methyl orange.

Normal Carbonate Alkalinity.—When phenolphthalein is used as an indicator, the titration with standard acid gives half of the normal carbonate alkalinity. Normal carbonate is present if the alkalinity to phenolphthalein is greater than zero, but less than the alkalinity to methyl orange.† If the phenol-

* Dissolve 0.05 gram of the sodium salt of erythrosine in 1 liter of freshly boiled distilled water.

† See Table XXXI (p. 712).

phthalein alkalinity is exactly equal to $\frac{1}{2}$ the methyl orange or erythrosine alkalinity, it is due entirely to normal carbonate. If the phenolphthalein alkalinity is less than $\frac{1}{2}$ the methyl orange alkalinity, normal carbonate expressed in terms of $CaCO_3$ is equal to twice the phenolphthalein alkalinity. If the phenolphthalein alkalinity is greater than $\frac{1}{2}$ the methyl orange alkalinity, the normal carbonate is equal to twice the difference between the methyl orange alkalinity and the phenolphthalein alkalinity. The carbonate, CO_2 as carbonate, and bound CO_2 can be calculated as follows:

Carbonate (CO_3) = 0.6 times the normal carbonate expressed in terms of $CaCO_3$.

Carbon dioxide (CO_2) as carbonate = 0.44 times the normal carbonate expressed in terms of $CaCO_3$.

Bound carbon dioxide (CO_2) is the sum of the CO_2 as carbonate and one-half that as bicarbonate.

Caustic Alkalinity (Hydroxide).—If hydroxide or caustic alkalinity is present, the alkalinity to phenolphthalein is greater than $\frac{1}{2}$ the alkalinity to methyl orange; the alkalinity is due entirely to hydroxide, if the phenolphthalein alkalinity is equal to the methyl orange alkalinity. If the phenolphthalein alkalinity is more than $\frac{1}{2}$ and less than all the methyl orange alkalinity, hydroxide, expressed in terms of $CaCO_3$, is equal to twice the phenolphthalein alkalinity minus the methyl orange alkalinity.

Bicarbonate Alkalinity.—Bicarbonate is present if the alkalinity to phenolphthalein is less than $\frac{1}{2}$ the alkalinity to methyl orange. The alkalinity to methyl orange is due entirely to bicarbonate, if there is no phenolphthalein alkalinity. If there is phenolphthalein alkalinity, the bicarbonate in terms of $CaCO_3$ is equal to the methyl orange alkalinity minus twice the phenolphthalein alkalinity. Bicarbonate, CO_2 as bicarbonate, and half-bound CO_2 can be calculated as follows:

Bicarbonate (HCO_3) = 1.22 times the bicarbonate expressed in terms of $CaCO_3$.

Carbon dioxide (CO_2) as bicarbonate = 0.88 times the bicarbonate expressed in terms of $CaCO_3$.

Half-bound carbon dioxide (CO_2) = 0.44 times the bicarbonate expressed in terms of $CaCO_3$.

Alkalinity Due to Sodium or Potassium Carbonates.—Waters from alkaline regions which contain alkali carbonates are found to contain all their Ca and Mg as carbonates or bicarbonates, *i.e.*, they possess either no non-carbonate hardness (sulfates, nitrates, or chlorides of Ca and Mg) or only traces of it. The most accurate method is to determine the total alkalinity by titration with 0.02 N H_2SO_4, using erythrosine indicator; then determine the Ca and Mg, and subtract from the total alkalinity the computed alkalinity due to the Ca and Mg, expressed in terms of $CaCO_3$. The remainder is the alkalinity due to carbonates of Na and K.

Table XXXI—Relations between Alkalinity to Phenolphthalein and to Methyl Orange

Result of Titration*	Value of Radical Expressed in Terms of $CaCO_3$		
	Hydroxide	Carbonate	Bicarbonate
$P=0$	0	0	T
$P<\frac{1}{2}T$	0	$2P$	$T-2P$
$P=\frac{1}{2}T$	0	$2P$	0
$P>\frac{1}{2}T$	$2P-T$	$2(T-P)$	0
$P=T$	T	0	0

* T = Total alkalinity in presence of methyl orange.
P = Alkalinity in presence of phenolphthalein.

Carbonic Acid.—General.—Carbonic acid may exist in water in 3 forms, namely, free CO_2, HCO_3 (bicarbonate) and CO_3 (carbonate). One-half of the CO_2 present as bicarbonate is known as the "half-bound" CO_2. The CO_2 of carbonate plus $\frac{1}{2}$ that of bicarbonate is known as the "bound CO_2."

Free CO_2.—If the water is acid to phenolphthalein and alkaline to methyl orange, measure 100 cc. of the sample into a tall, narrow vessel, preferably a 100-cc. Nessler tube, and titrate rapidly with N/22 Na_2CO_3 solution,* stirring gently until a faint pink color is produced with phenolphthalein. The number of cc. of N/22 solution gives the parts of free CO_2 per 100,000. Free CO_2 in terms of parts of $CaCO_3$ per 100,000 may be obtained by multiplying the previous figure by 2.274.

* 0.05 N Na_2CO_3 may be used for titrating. In this case multiply the number of cc. by 1.1 to obtain parts of free CO_2 per 100,000 (see also p. 695).

NOTES.—(1) The N/22 Na_2CO_3 solution is made by dissolving 2.41 grams of pure, dry Na_2CO_3 in 1 liter of distilled water which has been boiled and cooled in an atmosphere free from CO_2. Preserve the solution in bottles of resistant glass protected from the air by soda-lime. 1 cc. = 0.001 gram CO_2.

(2) N/44 NaOH solution may be used in place of N/22 Na_2CO_3. It is prepared in the same way as the 0.02 N NaOH solution described in the note after Total Acidity below, adjusting the concentration by titration so that the solution contains 0.909 gram of NaOH per liter. 1 cc. = 0.001 gram CO_2.

BICARBONATE AND CARBONATE.—The calculation of these has been previously described under Bicarbonate Alkalinity and Normal Carbonate Alkalinity.

Acidity.—In addition to free CO_2 water may contain mineral acids and various salts which give an acid reaction, particularly sulfates of Fe and Al.

TOTAL ACIDITY.—Add 4 drops of phenolphthalein indicator to 100 cc. of the sample in a white porcelain casserole or an Erlenmeyer flask over a white surface. Titrate with 0.02 N NaOH (see note) until the solution turns pink. The number of cc. of NaOH solution gives the total alkalinity in parts of $CaCO_3$ per 100,000. In the presence of $Al_2(SO_4)_3$ and certain other salts of this nature the determination is of questionable value, as the true end-point is reached with extreme slowness, if at all.

NOTE.—*0.02 N NaOH Solution.*—This solution should be carbonate-free. A solution sufficiently free from carbonates can be made by first preparing a saturated solution of NaOH and letting it stand stoppered for some time in a Pyrex glass flask. The Na_2CO_3, being insoluble in saturated NaOH solution, will settle to the bottom. The strength of the supernatant liquid can then be estimated by a preliminary titration and the solution then diluted to the proper strength (0.8002 gram NaOH per liter) with water which has been freed from CO_2 by boiling, and cooled in a CO_2-free atmosphere. This solution should be preserved in containers of resistant glass protected from the air by tubes filled with soda-lime. It should be standardized by titration against weighed portions of about 0.10 gram of pure benzoic acid,* which has been recently fused. (40 cc. 0.02 N NaOH = 0.09764 gram benzoic acid.) The benzoic acid is dissolved in a small quantity of alcohol and the titration made with phenolphthalein. In order to prevent interference of CO_2 of the air, the titration should be made rapidly or, preferably, a stream of CO_2-free air should be kept passing through the titration flask. A blank titration should be made on the alcohol and correction made for any acidity found. 1 cc. of the solution = 0.001 gram $CaCO_3$.

* See *Bur. Standards, Sci. Papers* 183, *Bull.* 8, 643–650 (1913).

Free Mineral Acid.—Add 2 drops of methyl orange indicator to 100 cc. of the sample in a white porcelain casserole or an Erlenmeyer flask over a white surface and titrate with 0.02 N NaOH until the pink color disappears. The number of cc. of the NaOH solution required gives directly the acidity expressed in parts of $CaCO_3$ per 100,000. This figure multiplied by 0.980 gives H_2SO_4 in parts per 100,000.

Note.—In the presence of appreciable amounts of Fe and Al salts this procedure gives results which are too high. In such cases determine the acidity due to mineral acids and sulfates of Fe and Al as described below and subtract from the result obtained the amount of acidity due to the Fe and Al salts as calculated from the amounts of these substances separately determined.

Mineral Acids and Sulfates of Fe and Al.—Modify the method given above for Free Mineral Acid by making the titration with phenolphthalein indicator at boiling temperature.

Note.—The Logwood test for alum or $Al_2(SO_4)_3$ in water is not reliable.

Hydrogen Sulfide.*—Transfer a suitable quantity of the sample to a graduated container by means of a siphon and add a few drops of phenolphthalein indicator. If alkaline, add HCl until the pink color disappears. Then add starch indicator and, with careful stirring, titrate with 0.01 N iodine solution until a permanent blue color appears. Correct for the quantity of iodine solution necessary to give an equal blue color with the same amount of distilled water and starch indicator.

Siphon 100–500 cc. of the sample, according to the H_2S content from the results of the preliminary determination, into a graduated vessel, keeping the outlet of the siphon below the liquid. Add immediately a sufficient amount of HCl, calculated from the approximate determination, to make neutral to phenolphthalein indicator. Mix carefully with a bent glass rod and immediately add about 0.5 cc. less of the 0.01 N iodine solution than is necessary to combine with the H_2S present. Add 5 cc. of starch indicator and finish the titration with the iodine solution, drop by drop with stirring, until a blue color remains permanently. Correct for the quantity of iodine solution needed to give an equal blue color when the same quantity of starch solution is

* *J. Assoc. Official Agr. Chem.*, **9**, 29 (1926).

added to an approximately equal volume of boiled and cooled distilled water. If possible make several determinations and take the average.

CALCULATION.—1 cc. 0.01 N iodine = 0.00017 gram H_2S.

Silica.—Evaporate 100–1000 cc. of the water to obtain if possible a residue of 0.4–0.6 gram, preferably containing 0.1–0.2 gram of Ca. (If a complete analysis is being made, the residue from the total solids may be employed.) When nearly dry, add 1 cc. of dil. HCl (1:1), moistening the sides of the dish, and evaporate to dryness. If much organic matter is present, char it in a radiator, as described on page 674. Moisten the residue with dil. HCl, evaporate most of the excess on the steam bath, take up in hot water and filter. Wash with hot water, ignite strongly, cool in a desiccator and weigh. (In case extreme accuracy is desired, the filtrate should be again evaporated to dryness with a little HCl to separate the small amount of SiO_2 which is not dehydrated by the first evaporation.)

The residue contains SiO_2 and may also contain certain bases combined as silicates, and $BaSO_4$, etc. Add 2 drops of conc. H_2SO_4 and a few cc. of HF, evaporate to dryness under the hood, expel SO_3 fumes by ignition, cool and weigh again. The loss is SiO_2. If the residue from the HF treatment exceeds 0.5 milligram, dissolve it in HCl and add to the original filtrate; if less than 0.5 milligram, report as Bases Combined with Silica.

NOTE.—For ordinary purposes the HF treatment is unnecessary. The original residue insoluble in HCl may be reported as Silicious Matter.

Iron Oxide and Alumina.—To the original filtrate from the SiO_2, add a few drops of conc. HNO_3 or Br water and boil down to about 100 cc. Add a slight excess of NH_4OH, boil for 1 minute, filter and wash with hot water. If there is considerable precipitate, dissolve it in hot dil. HCl and reprecipitate with NH_4OH in a volume of 25 cc.; filter and wash with hot water. Ignite strongly, cool in a desiccator and weigh. (If Al_2O_3 is not desired, omit the ignition.)

ALUMINA.—The precipitate contains Al_2O_3 and Fe_2O_3 (and P_2O_5, if present). Determine the Fe_2O_3 as below (and the P_2O_5 on a separate portion) and subtract to obtain the Al_2O_3.

IRON.—If the amount of Fe is considerable, fuse the above ignited residue with $KHSO_4$, dissolve in water, add sufficient

H_2SO_4 to make a 5% solution, pass through a Jones reductor and titrate with 0.1 N or 0.01 N $KMnO_4$. If the precipitate was not ignited, dissolve it through the filter paper with a hot 5% H_2SO_4 solution and then reduce and titrate. Calculate to Fe or Fe_2O_3, as desired.

CALCULATION.—1 cc. 0.1 N $KMnO_4$ = 0.008 gram Fe_2O_3.
= 0.0056 gram Fe.

In case the amount of Fe is small, determine it colorimetrically, as described on page 691, preferably on a separate portion of the sample. If it is desired to determine it on the NH_4OH precipitate, dissolve the latter in a definite quantity of HCl and make sure of oxidation by the addition of HNO_3, using in all about 1 cc. each of conc. HCl and HNO_3.

Lime.—Concentrate the filtrate from the Fe_2O_3 and Al_2O_3 to about 100 cc. and add to the hot ammoniacal solution a conc. solution of $(NH_4)_2C_2O_4$, very slowly. Let stand hot until the precipitate settles clear; filter and wash with hot water. (For extreme accuracy dissolve the CaC_2O_4 in a little hot dil. HCl and reprecipitate with NH_4OH and $(NH_4)_2C_2O_4$.) Ignite in a platinum crucible with a blast lamp, cool in a desiccator, and weigh as CaO; or titrate the CaC_2O_4 with 0.1 N $KMnO_4$ in the usual way (see under Lime, p. 697).

Magnesia.—The filtrate from the lime contains Mg and Mn. Acidify with HCl and concentrate to about 100 cc. Add a large excess of sodium or ammonium phosphate solution (or 20 cc. of saturated microcosmic salt solution). Cool and make slightly but distinctly alkaline with NH_4OH, added drop by drop. Stir thoroughly, let stand several hours, overnight if possible. Filter through a weighed Gooch crucible and wash with a 3% solution of NH_4OH. Place the crucible inside of a large platinum crucible, ignite strongly until white or light gray, cool in a desiccator, and weigh as $Mg_2P_2O_7$. Calculate to MgO.

CALCULATION.—$Mg_2P_2O_7 \times 0.3621 = MgO$.

NOTES.—(1) If Mn is present in the water, the ignited precipitate will also contain $Mn_2P_2O_7$ and must be corrected accordingly from the Mn content as determined below on a separate portion. ($Mn \times 2.585 = Mn_2P_2O_7$.)

(2) If extreme accuracy is desired, especially in the presence of considerable Na or K salts, the original $MgNH_4PO_4$ precipitate should be dis-

solved in a little dil. HCl and reprecipitated with NH_4OH and a few drops of phosphate solution.

Manganese.—The total Mn should be determined by the Bismuthate Method, if the water contains less than 1 part of Mn per 100,000. If it contains more, the Persulfate Method should be used. The bismuthate method will detect 0.02 milligram of Mn. For reliable results by this method the color comparisons should be made rapidly and the sample must be freed from organic matter and excessive chlorides.

Bismuthate Method.—*Reagents.*—(*a*) Standard $KMnO_4$ Solution.—Dissolve 0.2877 gram of purest $KMnO_4$ in about 100 cc. of distilled water. Acidify with H_2SO_4 and heat to boiling. Add slowly sufficient dil. $H_2C_2O_4$ solution to discharge the color. Cool and dilute to 1 liter. 1 cc. = 0.0001 gram Mn.

(*b*) Dilute HNO_3 (1:1).—Freed from oxides by blowing a current of air through it.

(*c*) Stronger H_2SO_4 (1:3).

(*d*) Dilute H_2SO_4.—Dilute 25 cc. of conc. acid to 1 liter and add enough $KMnO_4$ solution to obtain a faint but perceptible color.

(*e*) Sodium Bismuthate.—Pure, dry salt, free from Mn.

Procedure.—Use a volume of the sample which contains not over 0.0002 gram of Mn.* Add 0.5 cc. of dil. H_2SO_4 (1:3) and evaporate to dryness. Drive off SO_3 fumes by ignition. This removes organic matter and Cl. Dissolve the residue in 40 cc. of dil. HNO_3 (1:1), add 0.5 gram of sodium bismuthate and heat until the pink color disappears. Add a few drops of a solution of NH_4 or Na bisulfite to clear the solution and again boil to remove oxides of N. Then cool to 20° C. and again add 0.5 gram of sodium bismuthate. Stir a few minutes until the maximum color develops and filter through thoroughly ignited and washed asbestos in a Gooch crucible or through an alundum filter. Wash the precipitate with the dil. H_2SO_4 until the washings are colorless. Transfer the filtrate to a 50-cc. Nessler tube and make up to the mark. Compare its color with that

* If colloidal S, H_2S or other sulfides are present, evaporate to dryness in a porcelain dish on the water bath and treat the residue with 30 cc. of dil. HNO_3 (2:3). Again evaporate to dryness and repeat the evaporation with HNO_3 at least 3 times. Take up the final residue with 25 cc. of distilled water (see also footnote, p. 722).

of standards prepared from the standard $KMnO_4$ solution by taking portions of 0.2, 0.4, 0.6 cc., etc., of the standard solution, diluting and treating each in the same manner as the sample.

Persulfate Method.—*Reagents.*—(*a*) Dilute HNO_3 (1:1).—Prepared the same as for the Bismuthate Method above.

(*b*) $AgNO_3$ Solution.—20 grams dissolved in 1 liter of distilled water.

(*c*) Standard $KMnO_4$ Solution.—Prepared the same as for the Bismuthate Method.

(*d*) $(NH_4)_2S_2O_8$.—Crystals, free from Cl.

Procedure.—Use an amount of the sample which contains not over 0.0002 gram of Mn. Add 2 cc. of the dil. HNO_3 (1:1) and boil down to about 50 cc. Precipitate the Cl with $AgNO_3$ solution, adding at least 1-cc. excess. Shake and heat to coagulate the AgCl and filter. If the sample contains much Cl, it should be evaporated with a few drops of H_2SO_4 and heated until white fumes of SO_3 appear and then diluted before the HNO_3 and $AgNO_3$ are added. If the sample is highly colored by organic matter, it should be evaporated with H_2SO_4 and the residue ignited and dissolved in dil. HNO_3.

Add about 0.5 gram of $(NH_4)_2S_2O_8$ crystals and warm the solution until the maximum $KMnO_4$ color develops, which usually requires about 10 minutes. At the same time prepare standards by diluting portions of 0.2, 0.4, 0.6 cc., etc., of the standard $KMnO_4$ solution to about 50 cc. and treating them exactly like the sample. Transfer the sample and the standards to 50-cc. Nessler tubes, and compare the colors immediately.

Sulfur Trioxide.—Evaporate 100–1000 cc.* of the water, or sufficient to obtain 0.4–0.6 gram of residue and preferably 0.05–0.2 gram of Na. Acidify with HCl and remove the SiO_2 as previously described. Heat the filtrate to boiling and add a slight excess of hot $BaCl_2$ solution, drop by drop. Let stand overnight if possible, protected from SO_3 fumes, filter hot, and wash with boiling water. Ignite in a platinum crucible, cool in a desiccator, and weigh as $BaSO_4$. Calculate to SO_3.

Calculation.—$BaSO_4 \times 0.3430 = SO_3$.

Note.—If the sample is high in SO_3, especially if the Ca is also high, add to the filtrate from the SiO_2 an equal volume of conc. HCl and a slight excess

* If lithium is to be determined, evaporate 1–5 liters of the water.

of $BaCl_2$ solution. Evaporate to dryness, take up in water and a few drops of HCl, digest until the precipitate settles readily, filter, wash, and ignite.

Sodium, Potassium, and Lithium.—The filtrate from the SO_3 determination contains the Na, K and Li. Evaporate to dryness in a platinum dish and ignite the residue to faint redness to remove NH_4 salts. Dissolve the residue in about 200 cc. of water and precipitate with milk of lime or a saturated solution of $Ba(OH)_2$. Boil, let stand 30 minutes and filter. Wash the precipitate thoroughly with hot water and combine the filtrate and washings. If the precipitate of $Mg(OH)_2$ is large, dissolve it in a small amount of conc. HCl, evaporate to dryness, take up with water and reprecipitate as before. Concentrate the filtrates and washings to 200–250 cc. Add conc. NH_4OH and sufficient solid ammonium carbonate to precipitate the Ca and Ba. Let stand on the steam bath for 1–2 hours. Filter off the supernatant liquid, dissolve the precipitate in conc. HCl, reprecipitate as above and wash thoroughly with hot water. Evaporate the combined filtrates and washings to dryness and drive off the NH_4 salts by gentle heat. Treat the residue with water, filter through a small filter, using as little wash water as possible; evaporate to a small volume and again precipitate with 1 or 2 drops of conc. NH_4OH and 2 or 3 drops of saturated solutions of ammonium carbonate and oxalate. If any precipitate appears, filter and repeat the process.

Evaporate the filtrate to dryness and drive off all NH_4 salts by heating to faint redness in a platinum dish. Treat the residue with a little water. Filter into a small unweighed platinum dish, add a few drops of dil. HCl (1:1) and evaporate to dryness. Dry in the oven, heat to faint redness, cool in a desiccator and weigh as NaCl+KCl+LiCl. Repeat the heating to constant weight. Dissolve the mixed chlorides in hot water, filter and wash. Burn off the filter paper in the same dish, dry, ignite and weigh. The difference between the two weights gives the weight of mixed chlorides.

Lithium.*—Transfer the combined chlorides to a 50–100-cc. Erlenmeyer flask and evaporate the solution nearly, but not quite, to dryness. Add about 30 cc. of redistilled amyl alcohol. Remove the water by connecting the flask, the stopper of which

* If lithium is not desired, proceed as under Potassium below.

carries a thermometer, with a condenser and boiling until the temperature rises to the boiling point of amyl alcohol (approximately 130° C.) Cool slightly and add a drop of dil. HCl (1:1) to convert small quantities of LiOH to LiCl. Connect with the condenser and repeat the boiling until the temperature reaches the boiling point of amyl alcohol to again drive off the water. (The contents of the flask at this time are usually 15–20 cc.) Filter through a small paper or a Gooch crucible into a graduated cylinder and note the exact quantity of the filtrate, as this determines the subsequent correction. Wash the precipitate with small quantities of amyl alcohol. If the quantity of lithium exceeds 2 or 3 milligrams, dissolve the precipitate in the flask and on the filter with hot water and repeat the separation by boiling again in amyl alcohol. Filter and wash as before, noting the exact quantity of filtrate exclusive of washings. Evaporate the filtrates and washings in a small platinum dish to dryness on the steam bath, dissolve the residue in water, and add a few drops of dil. H_2SO_4 (1:1). Evaporate on the steam bath and expel the excess of H_2SO_4 by heating gently over a burner until the carbonaceous matter is completely burned off, repeating the addition of a few drops of the H_2SO_4 if necessary. Cool and weigh the dish and contents. Dissolve in a small quantity of hot water, filter through a small filter, wash, return the filter to the dish, ignite, and weigh. The difference between the two weights is the weight of impure Li_2SO_4.

Test the purity of the Li_2SO_4 by adding small quantities of 10% $(NH_4)_2HPO_4$ solution and conc. NH_4OH, which will precipitate any Mg present in the sulfate. Let stand overnight and if a precipitate forms, collect on a small filter, wash with 3% NH_4OH, ignite and weigh as $Mg_2P_2O_7$. Calculate this to $MgSO_4$ and subtract from the weight of the impure Li_2SO_4. From this weight also subtract 0.00113 gram for every 10 cc. of amyl alcohol filtrates, exclusive of the amyl alcohol used in washing the residue, to correct for the solubility of NaCl and KCl in amyl alcohol. Calculate the corrected weight of Li_2SO_4 to Li or Li_2O as desired.

CALCULATIONS.—$Mg_2P_2O_7 \times 1.0812 = MgSO_4$.

$Li_2SO_4 \times 0.2656 = Li_2O$.

$Li_2SO_4 \times 0.1262 = Li$.

Potassium.—Dissolve the mixed chlorides from the flask in the lithium determination (or the original mixed chlorides without separation of the Li) in hot water and filter. Evaporate to dryness, ignite gently to remove amyl alcohol, wash thoroughly, and concentrate the filtrates and washings to 25–50 cc. Transfer to a porcelain dish and add 1 cc. of 10% $PtCl_4$ solution for each 0.03 gram of the combined chlorides. Evaporate to dryness and treat the residue with 80% by volume alcohol. Filter and wash with 80% alcohol until the filtrate is no longer colored. Dry the filter containing the precipitate, dissolve the latter in hot water and transfer to a weighed platinum dish. Evaporate on the steam bath, dry in the oven for 30 minutes at 100° C., and weigh as K_2PtCl_6. Calculate to KCl. To the weight of KCl obtained, add 0.00051 gram for every 10 cc. of amyl alcohol used in the extraction of the LiCl to correct for the solubility of KCl in amyl alcohol. Calculate the corrected weight of KCl to K or K_2O as desired.

Calculations.—$K_2PtCl_6 \times 0.3067 = KCl.$
$KCl \times 0.5244 = K.$
$KCl \times 0.6317 = K_2O.$

Note —The ignition of the mixed chlorides to remove amyl alcohol and the correction applied to the weight of KCl are of course unnecessary if Li is not determined. In such cases the Na as calculated below includes the Li.

Sodium.—Subtract the combined corrected weights of LiCl and KCl from the total weight of the mixed chlorides, originally obtained above, to obtain the weight of NaCl, and calculate this to Na or Na_2O as desired.

Calculations.—$NaCl \times 0.3934 = Na.$
$NaCl \times 0.5303 = Na_2O.$

Note.—If it is not desired to separate Na and K, the combined chlorides may be considered as NaCl and calculated to Na_2O or Na.

Bromine, Iodine, Arsenic, and Boron

General.—Evaporate to dryness a large amount of the water, preferably 2 liters, after making slightly alkaline with Na_2CO_3. Boil the residue thus obtained with distilled water, transfer to a

filter and thoroughly wash with hot water.* Make the alkaline filtrate up to a definite volume and determine the constituents specified in aliquot portions.

Iodine.—Evaporate to dryness an aliquot of the alkaline filtrate (equivalent to at least 500 cc. of the original water), add 2–3 cc. of water to dissolve the residue and enough 95% alcohol to make the percentage of alcohol about 90. This precipitates the chlorides. Heat to boiling, filter and repeat the treatment of the residue with water and 90% alcohol once or twice. Add 2–3 drops of 10% NaOH solution to the combined alcoholic filtrates and evaporate to dryness. Dissolve this last residue in 2–3 cc. of water and repeat the precipitation with alcohol, heating and filtering. Add a drop of 10% NaOH solution to the alcoholic filtrate and evaporate to dryness. Dissolve the residue in a little water, acidify with dil. H_2SO_4 (1:5), using 3–4 drops in excess, and transfer to a small flask. Add 4 drops of KNO_2 (not KNO_3) solution (2 grams per liter) and about 5 cc. of CS_2, freshly distilled. Shake until all the iodine is extracted and filter off the acid solution from the CS_2. Wash the flask, filter paper and contents with cold water and transfer the CS_2 containing the iodine to a Nessler tube, using about 5 cc. of the CS_2. In washing the filter, make the contents of the tube to definite volume, usually 12–15 cc., and compare the color with that of other tubes containing known amounts of iodine dissolved in CS_2. Prepare the standard tubes by treating measured quantities of a solution of known KI content as described above, beginning with "acidify with dil. H_2SO_4 (1:5)."

Bromine.—Transfer separately to small flasks the acid solution of the sample and the standards from which the iodine has been removed. To the standards add definite measured quantities of a KBr solution of known strength and to each of the flasks containing the sample and standards add 5 cc. of purified CS_2. Add freshly prepared saturated Cl water, 1 cc. at a time, shaking after each addition until all the Br is set free. Avoid a large excess of Cl, since a bromo-chloride may form and spoil the color reaction.

* The residue on the filter may be used for the determination of Mn (p. 717).

Filter off the water solution from the CS_2 through a moistened filter, wash the contents of the filter two or three times with water and then transfer to a Nessler tube by means of about 1 cc. of CS_2. Repeat this extraction of the filtrate twice, using 3 cc. of CS_2 each time. The combined CS_2 extracts usually amount to 11.5—12 cc. Add sufficient CS_2 to bring each tube to a definite volume, usually 12–15 cc., and compare the sample with the standards.

NOTES.—(1) In some cases where the Br is near the upper limits of the method, it is not all extracted by the amounts of CS_2 specified. In such cases make 1 or 2 extra extractions with CS_2, transfer the extracts to another tube and compare the color with some of the lower standards. Add the readings thus obtained to the others.

(2) Sufficiently accurate results for all ordinary purposes may be obtained on most samples by omitting the extractions with alcohol (which removes the chlorides), and by comparing the color of the CS_2 solutions directly in the extraction flasks, thus shortening the procedure.

Arsenic.—Evaporate to dryness an aliquot portion of the alkaline filtrate previously described. Acidify with As-free dil. H_2SO_4 (1 : 5) and determine the As in the Marsh apparatus, comparing with standard mirrors (see p. 51).

NOTE.—Mirrors may be conveniently prepared from aliquots of a solution made by dissolving 0.0132 gram of pure As_2O_3 in 100 cc. of water containing about 0.050 gram of Na_2CO_3. 1 cc. of this solution = 0.0001 gram of As.

Boron (Qualitative Test).—Evaporate to dryness a portion of the alkaline filtrate previously described. Treat with 1–2 cc. of water and slightly acidify with dil. HCl (1 : 1). Add about 25 cc. of 95% alcohol, boil, filter, and repeat the extraction of the residue. Make the filtrate slightly alkaline with NaOH and evaporate to dryness. Add a little water, *slightly* acidify with dil. HCl (1 : 1) and place a strip of turmeric paper in the liquid. Evaporate to dryness on the steam bath and continue heating until the turmeric paper is dry. If boric acid is present, the paper will become cherry-red, which will turn to greenish-black when moistened with Na_2CO_3 solution or a drop of dil. NH_4OH.

NOTES.—(1) It is not usually necessary to determine boron quantitatively but, if desired, the method of Gooch may be used. (See *Am. Chem. Jour.*, **9**, 23 (1887).)

(2) Glassware containing boron must not be used.

REFERENCES.—American Public Health Association: "Standard Methods of Water Analysis" (1925); Association of Official Agricultural Chemists: "Methods of Analysis" (1925).

COPPER, LEAD, TIN, AND ZINC IN WATER

General.—These determinations are of importance in mining regions and in connection with the solvent action of some waters upon pipes and other containers. It is possible to make a rough estimate of the amount of Pb present in clear waters by acidifying with acetic acid, saturating with H_2S and comparing the color produced with that of standard Pb solutions contained in Nessler tubes. This method, however, is not applicable when the water is colored or contains Fe. In such case proceed as follows:

Reagents.—The following special reagents are necessary:

(*a*) *Standard Pb Solution.*—Dissolve 1.60 grams of $Pb(NO_3)_2$ in 1 liter of distilled water. 1 cc. = 0.001 gram Pb. As a check determine the Pb in an aliquot by adding a little $HC_2H_3O_2$, precipitating with $K_2Cr_2O_7$ solution and weighing the $PbCrO_4$ (see p. 268). $PbCrO_4 \times 0.6411 = Pb$.

(*b*) *Standard Cu Solution.*—Dissolve about 0.8 gram of clean $CuSO_4 \cdot 5H_2O$ in water, add 1 cc. of conc. H_2SO_4 and dilute to 1 liter. In 100 cc. of this solution determine the Cu in the usual way by electrolysis (see p. 182). Dilute the solution so that 1 cc. contains 0.0002 gram of Cu.* This solution is permanent.

(*c*) *Ammonium Chloride.*—25% solution.

(*d*) *Ammonium Acetate.*—50% solution.

(*e*) *Potassium Sulfide Reagent.*—An alkaline solution of K_2S made by mixing equal volumes of 10% KOH solution and a saturated solution of H_2S in water.

(*f*) *Urea Crystals.*

Lead.—Concentrate rapidly by boiling in a 7-inch porcelain dish over a free flame 3–4 liters (or more) of the sample to a volume of about 30 cc. Add 10–15 cc. of the 25% NH_4Cl solution, then a few drops of conc. NH_4OH and saturate with H_2S water. Let stand for some time, preferably overnight. Add a little more NH_4OH and H_2S water, boil for a few moments

* For most purposes it is sufficiently accurate to weigh out 0.786 gram of the $CuSO_4 \cdot 5H_2O$ and dissolve to 1 liter without analyzing.

and filter. The precipitate contains all the Pb, Zn, Cu, and Fe as sulfides, also suspended organic matter. The soluble coloring matter passes into the filtrate.

Wash the precipitate once or twice with hot water. Return the precipitate and the filter paper to the original dish and boil with 50 cc. of dil. HNO_3 (1 : 9), rubbing the sides of the dish with a bit of filter paper if necessary to detach any adhering sulfide. Filter and wash free from acid with hot water. Evaporate the filtrate and washings in the original dish to about 10–15 cc. Cool, add 5 cc. of conc. H_2SO_4 and heat until copious SO_3 fumes appear.

If Pb is present, dilute the contents of the dish slightly with water, transfer to a beaker and treat with 150 cc. of 50% alcohol to render the $PbSO_4$ insoluble. Let stand some time, preferably overnight, filter and wash with 50% alcohol. Save the filtrate for the determination of Zn.

Dissolve the $PbSO_4$ by boiling the filter containing it in ammonium acetate solution in a porcelain dish. Filter into a 50-cc. Nessler tube, washing with boiling water containing a little ammonium acetate. Halve this filtrate and treat $\frac{1}{2}$ with saturated H_2S water to get an approximation of the Pb present. To the other half (or an aliquot, if a large amount is present) add a few drops of $HC_2H_3O_2$, then an excess of saturated H_2S water and compare the color obtained with a set of standards made by treating known amounts of the standard Pb solution with a little $HC_2H_3O_2$, ammonium acetate and H_2S.

Zinc.*—If Pb and Cu are known to be absent and Zn alone is to be determined, dilute the contents of the dish slightly, after having evaporated with H_2SO_4; add excess of NH_4OH to precipitate Fe, boil and filter. Acidify the filtrate slightly with H_2SO_4, concentrate to about 150 cc. and transfer to a weighed platinum dish. Add 2 grams of pure $K_2C_2O_4$ crystals and 1.5 grams of pure K_2SO_4. Connect the dish with an electrolytic current of about 0.3 ampere and electrolyze for 3 hours, or until the Zn is completely deposited. With the current still on, siphon off the solution in the dish and at the same time run in a

* Since the reagents used in this determination often contain traces of Zn, it is advisable to make a blank determination with each new lot of reagent, and correct the results if necessary.

stream of distilled water to replace the free acid. When no longer acid, break the current, remove the dish, wash with distilled water, then with 95% alcohol, dry at 70° C., cool and weigh. The increase in weight of the dish is metallic Zn.

If Zn is present and Cu is absent, concentrate the filtrate from the $PbSO_4$ to expel the alcohol and remove the Fe by adding an excess of NH_4OH. Boil, filter, wash, and slightly acidify the filtrate with H_2SO_4. Concentrate to about 150 cc. and determine Zn by electrolysis as above.

If Cu also is present, concentrate the filtrate from the $PbSO_4$ until alcohol is expelled, add an excess of NH_4OH, boil, filter out the iron precipitate, neutralize the filtrate with H_2SO_4 and then add 2 cc. of conc. H_2SO_4 and 1 gram of urea. Electrolyze the solution and determine Cu colorimetrically as described later. After the Cu has been deposited, add NH_4OH to the solution containing the Zn until nearly all the H_2SO_4 has been neutralized. Concentrate to slightly less than the capacity of the platinum dish. Add 1.5 grams of K_2SO_4 and 2 grams of $K_2C_2O_4$ crystals, and electrolyze for Zn as above. Since this solution is usually saturated with NH_4 salts, it is frequently impossible to get the Zn deposited firmly on the dish before the salts interfere by crystallization. To avoid this difficulty dilute $\frac{1}{2}$ the solution and electrolyze it for Zn; or, if the amount of Zn is very small, precipitate it as ZnS in acetic acid solution, wash on a filter paper, ignite in a small weighed porcelain crucible with free access of air, cool and weigh as ZnO. This difficulty will not be encountered if Cu is absent, as there will then be no excess of NH_4 salts.

Copper.—For waters containing 0.01–0.1 part of Cu per 100,000, take 1 liter and for other concentrations proportionate amounts. Evaporate to about 75 cc. and wash into a 100-cc. platinum dish. Add 2 cc. of dil. H_2SO_4 for clear soft waters. For alkaline waters add an additional amount to offset the alkalinity. For waters carrying much organic matter or clay, add 5 cc. of the acid. Connect the dish as the anode for electrolysis, suspending in it for a cathode a stout platinum wire about 50 cm. long, 40 cm. of which are coiled into a flat spiral. Have the spiral parallel to the bottom of the dish and about 0.5 inch above it. Electrolyze for about 4 hours with occasional stirring or preferably overnight, using a current of about 0.02 ampere through the solution.

Lift out the cathode without turning off the current and immerse the spiral in a small amount of boiling dil. HNO_3.

Wash off the wire and evaporate the HNO_3 solution to dryness on the water bath in a small porcelain dish. If Ag is suspected to be present, add a few drops of HCl before evaporation. Dissolve the residue in water and wash into a 50-cc. Nessler tube. Dilute to the mark and add 10 cc. of the K_2S reagent (*e*). The color of the CuS develops at once and is fairly permanent, lasting for several hours. Add 10 cc. of the K_2S solution to a similar tube containing 50 cc. of distilled water and then add to it standard Cu solution (*b*) in 0.2-cc. portions until the colors of the 2 tubes match. If 1 liter of the sample is used, the Cu in parts per 100,000 is equal to twice the number of cc. of the standard Cu solution required to match the color of the sample.

Tin.—Small quantities of Sn are occasionally found in waters that have passed through tin or tin-lined pipes. This metal, if present, is removed with the Fe by NH_4OH in the separation of Pb, Zn, and Cu. In the method for Cu alone it is removed in the same way and may be further avoided by dissolving the sulfides in conc. HNO_3, when any Sn present will be separated as an insoluble compound which may be ignited and weighed as SnO_2. There is as yet no satisfactory method for the quantitative separation of such small quantities of Sn but an approximate estimate may be obtained by following the method for determination of Sn in canned goods (see p. 522).

Reference.—The above procedures are essentially those of the American Public Health Association as published in 1925.

IRRIGATING WATER

General.—Determine the total solids in solution, chlorine, carbonic acid, bicarbonic acid, sulfur trioxide, lime, and magnesia by the methods described under Industrial Water and the Mineral Analysis of Water. Calculate the lime and magnesia to the acid radicals in the following order: bicarbonate, sulfate, and chloride; then calculate the remaining acid radicals, including carbonate, to the corresponding salts of sodium.

Black Alkali.—Reagent.—(*a*) *0.02 N Sodium Carbonate.*—1 cc. of this solution is equivalent to 0.00106 gram of Na_2CO_3.

(*b*) *0.02 N Sulfuric Acid.*—1 cc. of this solution is equivalent to 0.00100 gram of $CaCO_3$ or 0.00136 gram of $CaSO_4$.

(*c*) *Erythrosine Indicator.*—Dissolve 0.25 gram of the Na salt in 1 liter of water.

(*d*) *Chloroform.*—Neutral to erythrosine.

Determination.—Transfer 200 cc. of the water to a platinum or silver dish, add 50–100 cc. of 0.02 N Na_2CO_3, according to the amount of soluble salts of Ca and Mg present, and evaporate to dryness. Rub up the residue with CO_2-free water.* Transfer to a 100-cc. volumetric flask, make up to the mark, shake thoroughly, and let stand until clear (12–15 hours). Remove 50 cc. of the clear, supernatant liquid, equivalent to $\frac{1}{2}$ of the original quantity of water and Na_2CO_3 added, and transfer to a stoppered titrating bottle, of 250-cc. capacity, of clear glass without any tinge of pink. Add 5 cc. of the $CHCl_3$ and 1 cc. of the erythrosine and titrate with the standard acid until the color disappears. Shake the solution vigorously after each addition of the acid; the $CHCl_3$ produces a milky appearance which makes the reading of the end-point sharp and certain.

(1) If *less* H_2SO_4 is required than is equivalent to $\frac{1}{2}$ of the Na_2CO_3 added, due to some of the Na_2CO_3 reacting with soluble salts of Ca and Mg, the solution originally contained no black alkali in excess but rather an excess of the so-called permanent or non-carbonate hardness. It is customary to express the hardness in terms of $CaCO_3$ or $CaSO_4$. With irrigating waters the latter form is to be preferred. Therefore, the difference between the number of cc. of the H_2SO_4 required and $\frac{1}{2}$ of the number of cc. of the Na_2CO_3 added, multiplied by the factor 0.00136, gives the equivalent of $CaSO_4$ in 100 cc. of the water. Report as parts per 100,000.

(2) If *more* H_2SO_4 is required than that equivalent to $\frac{1}{2}$ of the Na_2CO_3 added, black alkali was originally present in the solution and the difference in cc., multiplied by the factor 0.00106, gives the black alkali in terms of Na_2CO_3 in 100 cc. of water. Report as parts per 100,000.

* For this purpose distilled water should be vigorously boiled until approximately one-third of the original volume is evaporated, then cooled and stoppered. An ordinary laboratory wash bottle should not be used to transfer the residue, as the CO_2 from the breath of the operator is sufficient to vitiate the results.

REFERENCE.—Association of Official Agricultural Chemists: "Methods of Analysis," 108 (1925).

SOILS

General.—The following procedures are essentially the Tentative Methods of the Association of Official Agricultural Chemists,* unless otherwise indicated. Report all results as percentages of the air-dried sample.

Directions for Sampling.—Sampling should be done preferably when the soil is reasonably dry. Remove from the surface all vegetable material not incorporated with the soil. With a soil auger or tube, whichever may be better adapted to the soil conditions, take a sufficient number of subsamples at properly distributed points to secure composite samples representative of the entire tract. Take a composite sample representative of the entire tract to the average depth of plowed soil, usually about 7 inches, and also a composite sample from each important and distinctly different soil stratum below the surface section already sampled, to a total depth of 40 inches. If a soil auger is used, before boring below the plowed depth enlarge the first boring and carefully clean out the hole to prevent contamination of the several substrata while withdrawing samples.

Mix the composite samples of each depth thoroughly and, after quartering down to about 2–4 pounds, air-dry in a cool, well-ventilated place.

It is recommended that the weight of a given volume of the soil as it lies in the field be taken for calculating the percentage results obtained by analysis to pounds per given area of the soil.

Preparation of Sample.—Prepare the laboratory samples by pulverizing in a porcelain pebble-mill or porcelain mortar, using a rubber-tipped pestle to avoid grinding of rock fragments, and pass it through a sieve with circular openings 1 mm. in diameter. Weigh and discard the detritus. Thoroughly mix the sifted material and preserve in a well-stoppered container. If necessary for the determination of any of the constituents, prepare a very finely pulverized subsample of the sifted material by grinding in an agate mortar.

* "Methods of Analysis." 21–34 (1925).

Moisture.—Dry 2 or more grams in a wide-mouthed weighing bottle at 100° C. to constant weight. Stopper while weighing. Report the loss of weight as Moisture.

Loss on Ignition.—Ignite the soil from the above determination to full redness, occasionally stirring, until organic matter is destroyed. If the soil contains appreciable quantities of carbonates, cool and moisten with a few drops of a saturated solution of ammonium carbonate; dry and heat to dull redness to expel NH_4 salts. Cool in a desiccator and weigh.

NOTE.—This gives only a crude approximation of the organic matter.

Total Nitrogen.—Digest 10 grams of the soil in a 500-cc. Kjeldahl digestion flask with 30–40 cc. of conc. H_2SO_4 and 0.7 gram of HgO or 0.65 gram of Hg. Mix immediately by shaking to prevent sticking to the sides of the flask. Heat over a low flame, increase the heat gradually, and rotate the flask frequently or shake if necessary to prevent the contents from caking on the bottom. Continue the digestion until the mixture is colorless or nearly so. After cooling, dilute the contents of the flask with about 100 cc. of water, add 25 cc. of K_2S solution (40 grams of K_2S* in 1 liter of water) and an excess of strong NaOH solution (about 1 : 1). Connect the flask with a distilling apparatus, mix the contents thoroughly and complete the determination as described under the Kjeldahl Method (p. 87).

NOTE.—If trouble is experienced from bumping, the distillation may be conducted in a copper flask, in which case transfer the mixture to it from the Kjeldahl flask before adding the K_2S and NaOH.

Nitrate Nitrogen.—Place 100 grams of air-dry soil and 500 cc. of water in a suitable container and agitate for 5 minutes. Add 1 gram of CaO or 2 grams of precipitated $CaCO_3$, agitate thoroughly, let settle for 10–20 minutes, and filter, making sure that a clear filtrate is obtained. If the filtrate contains 0.6 part of Cl per 100,000 or less, proceed as in the Phenoldisolfonic Acid Method for Nitrate Nitrogen in Water (p. 682), using 25 cc. of the filtrate. If it contains more than 0.6 part of Cl per 100,000, proceed as in the Reduction Method (p. 683), using 25 cc., or such a quantity as will not exceed 0.0001 gram of N in the form of nitrate. Report as percentage of Nitrate Nitrogen.

* 80 grams of $Na_2S_2O_3 \cdot 5H_2O$ may be used instead of the K_2S.

Phosphorus.—Place 5 grams of the soil in a porcelain dish. Moisten with 5–7 cc. of $Mg(NO_3)_2$ solution (see below). Dry on the water bath and burn off the organic matter at low redness. Cool and add 10 cc. of water, 10 cc. of conc. HCl and 5 cc. of conc. HNO_3. Cover the dish and digest for 2 hours on the water bath, stirring two or three times during the digestion. Transfer to a 250-cc. volumetric flask, cool, dilute to the mark, mix well and pour through a dry folded filter, pouring back on the filter until the solution runs through clear. Pipette an aliquot corresponding to 2 or 4 grams of the soil, depending upon its P_2O_5 content, into a porcelain dish and evaporate to dryness. Take up with dil. HNO_3 (1 : 4), again evaporate to dryness and heat for 1 hour at 110–120° C. Again take up with dil. HNO_3 and filter. Evaporate the filtrate and washings to 30–40 cc. Make alkaline with NH_4OH and dissolve the precipitate with conc. HNO_3, using a slight excess. Add gradually, with vigorous shaking, 15 cc. of molybdate solution (see below). Keep the solution at 40–50° C. for 1 hour and let stand overnight at room temperature. Filter and wash the flask and the precipitate *thoroughly* with cold water. (It must be washed *free from acid.*) Return the filter and precipitate to the same flask and determine the P_2O_5 volumetrically as follows: Dissolve the yellow precipitate in a measured excess of standard NaOH or KOH solution, add a few drops of phenolphthalein solution and titrate the excess of alkali with standard HNO_3. Calculate the alkali consumed to P_2O_5. 1 cc. of the standard alkali should be made to equal 0.0005 gram of P_2O_5.

Solutions.—(*a*) *Magnesium Nitrate.*—Dissolve 160 grams of calcined MgO in dil. HNO_3 (1:1), avoiding an excess of the acid; then add a little of the MgO in excess, boil, filter and dilute to 1 liter.

(*b*) *Molybdate Solution.*—Dissolve 100 grams of MoO_3 in a mixture of 144 cc. of conc. NH_4OH and 271 cc. of water. Pour the solution slowly and with constant stirring into a mixture of 489 cc. of conc. HNO_3 and 1148 cc. of water. Keep in a warm place for several days or until a portion heated to 40° C. gives no yellow precipitate. Decant from any sediment and preserve in glass-stoppered bottles.

(*c*) *Standard Alkali.*—Dilute 161.9 cc. of normal NaOH or KOH, which has been freed from carbonates, to 1 liter. 100 cc. of this solution should neutralize 32.38 cc. of 0.5 N acid.

(*d*) *Standard HNO_3.*—This should be of about the same strength as the alkali and carefully standardized against it with phenolphthalein.

Silica.—Thoroughly mix on glazed paper 5 grams of soil, ground to an impalpable powder, with 25 grams of Na_2CO_3. Transfer carefully to a 100-cc. platinum or nickel crucible, cover, heat at low redness until fusion begins, then increase the heat until a clear, quiet fusion results. Finally, give the full heat of a Meker burner for 20 minutes, having the flame oblique to insure good oxidation. Pour the fusion into a large platinum dish set in water. Place the crucible and cover in a wide 400-cc. beaker. Cover with water, transfer the fused lump from the platinum dish to the beaker and rinse the dish with dil. HCl (1:9) into the beaker. Add 50 cc. of conc. HCl to the contents of the beaker, cover, and place upon the steam bath until the fused mass has disintegrated. Transfer the mixture to the platinum dish and evaporate to dryness on the steam bath.

Take up the residue in dil. HCl (1:9) and filter. (A 9-cm. Büchner funnel with suction will be found convenient.) Wash with hot water containing 5 cc. of conc. HCl per liter. Collect the filtrate and washings in a dish, preferably a casserole, and dehydrate on the steam bath until the SiO_2 assumes a crystalline appearance. Moisten with conc. HCl and repeat the dehydration for 2 hours. Add 5 cc. of conc. HCl and 100 cc. of hot water. Mix thoroughly, filter and wash. Add the residue to the main portion of SiO_2 obtained from the first filtration. Make up the combined filtrate and washings to 500 cc. at 20° C. and save for subsequent determinations. Place the two SiO_2 residues with filters in a weighed crucible, and moisten with saturated NH_4NO_3 solution. Ignite slowly at first to burn off the filter paper and then with a strong flame, preferably a blast lamp, to constant weight. Cool in a desiccator and weigh as SiO_2.

Iron, Aluminum and Titanium Oxides.—To an aliquot of the solution from the SiO_2 determination (100 or 200 cc., according to the probable amount of Fe and Ca present) add dil. NH_4OH (1:1), drop by drop, until the precipitate formed requires several

seconds to dissolve, thus leaving the solution faintly acid. Heat nearly to boiling and add sufficient dil. NH_4OH to precipitate all Fe, Al, etc. Let boil in a covered beaker for about 1 minute, remove, and if no NH_3 is given off (detect by smell), add more, drop by drop, until it can be detected. Do not let the precipitate settle, but stir and pour upon the filter. Wash immediately with hot 2.5% NH_4NO_3 solution, playing a fine jet round the edge of the precipitate, thus cutting it free from the paper in order to produce rapid filtration. Wash the precipitate several times and return it to the original beaker. Dissolve with a few drops of conc. HCl and warm. Reprecipitate the Fe, Al and P_2O_5 with dil. NH_4OH as above, filter and wash until free from Cl with hot 2.5% NH_4NO_3 solution. Reserve the filtrate and washings from both precipitations for the determination of Lime and Magnesia.

Dry the precipitate, remove from the filter paper, ignite the latter separately in a weighed platinum crucible and then add the precipitate to the crucible. Ignite to bright redness, cool in a desiccator and weigh as $Fe_2O_3+Al_2O_3+TiO_2+P_2O_5$. To this residue add $KHSO_4$ and heat at a low temperature until the precipitate is completely disintegrated. When solution is complete, cool quickly and transfer to a flask containing 100 cc. of dil. H_2SO_4 (1:3). After complete solution of the melt reduce with Zn in a Jones reductor, cool, titrate with 0.1 N $KMnO_4$ solution and calculate to Fe_2O_3.

Subtract the Fe_2O_3, together with the P_2O_5 (separately determined as previously described), from the collective weight of mixed oxides and report the remainder as Aluminum and Titanium Oxides.

NOTES.—(1) For the small amounts of TiO_2 present in soils, the above procedure is usually sufficiently accurate. If it is desired to determine the TiO_2, it may be done colorimetrically on a separate aliquot of the original solution from the SiO_2 (see p. 778).

(2) The Fe_2O_3 may also be determined directly on a separate 50 or 100 cc. of the original solution. Add 5 or 10 cc. of conc. H_2SO_4, evaporate to fumes of SO_3 to drive off all HCl, cool, dilute with water, reduce with Zn, and titrate with $KMnO_4$ solution.

Lime.—Evaporate the filtrate and washings from the NH_4OH precipitate above to about 50 cc., cool, add $(NH_4)_2S$, filter off

the MnS and wash with hot water. Again evaporate to about 50 cc., make slightly alkaline with NH_4OH and add, while still hot, saturated $(NH_4)_2C_2O_4$ solution, drop by drop, slightly in excess, to convert the Mg salts also into oxalate. Heat to boiling, let settle completely (3 hours or longer), decant the clear solution through a filter, pour 15–20 cc. of hot water on the precipitate and again decant the clear solution through the filter. Dissolve the precipitate in the beaker with a few drops of conc. HCl, add a little water and reprecipitate boiling hot by adding NH_4OH to slight alkalinity and a little $(NH_4)_2C_2O_4$ solution. Let stand as before and filter through the same filter. Wash free from Cl with hot water. Dry, ignite over a blast lamp until it ceases to lose weight, cool in a desiccator and weigh as CaO. Save the filtrate and washings for the MgO determination.

NOTE.—The CaC_2O_4 may be titrated with 0.1 N $KMnO_4$ in the usual way, instead of igniting it (see p. 697).

Magnesia.—Evaporate the filtrate and washings from the CaO determination to about 100 cc. on the water bath and add cautiously 20 cc. of conc. HNO_3. Evaporate to dryness and carefully heat on a hot plate to expel NH_4 salts. Add 5 cc. of conc. HCl and evaporate nearly to dryness. Dissolve in hot water and a little conc. HCl. If necessary, filter and wash with about 100 cc. of hot water. Add 3 cc. of 10% $(NH_4)_2HPO_4$ solution and sufficient NH_4OH with constant stirring to make the solution slightly alkaline. Stir vigorously and let stand 15 minutes. Then add 15 cc. of conc. NH_4OH, cover and let stand overnight. Filter through a weighed porcelain Gooch crucible, wash the precipitate free from Cl with dil. NH_4OH (1:9), and dry. Heat at first at a moderate heat, then ignite intensely until white or grayish white and weigh as $Mg_2P_2O_7$. Calculate to MgO.

CALCULATION.—$Mg_2P_2O_7 \times 0.3621 = MgO$.

Manganese.—REAGENTS.—The reagents are those employed in the Bismuthate Method for the determination of Mn in water (p. 717).

DETERMINATION.—Treat 1 gram of the original soil in a platinum dish with about 5 cc. of HF, 5 cc. of water and 5 cc. of dil. H_2SO_4 (1:3). Evaporate to dryness, ignite and fuse the residue with $KHSO_4$. Dissolve in water in a beaker, add conc. HNO_3 and evaporate to dryness. Again dissolve in water, add 25 cc. of

dil. HNO_3 (1:2) and about 0.5 gram of sodium bismuthate, and heat until the permanganate color disappears. Add a few drops of a solution of NH_4 or Na bisulfite to clear the solution and again boil to expel oxides of N. Remove from the source of heat, cool to 20° C., again add 0.5 gram of sodium bismuthate and stir. When the maximum permanganate color has developed, filter through an alundum or Gooch crucible containing an asbestos mat which has been ignited and washed with 4% $KMnO_4$ solution and then with water. Wash the precipitate with the dil. H_2SO_4 until the washings are colorless. Transfer the filtrate to a colorimeter tube and compare its color with that of standards prepared from the standard $KMnO_4$ solution by taking portions of 0.2, 0.4, 0.6 cc., etc., of the $KMnO_4$ solution, treating with sodium bismuthate and diluting with the dil. H_2SO_4 to the same volume as the filtrate from the sample. Report as percentage of Manganomanganic Oxide, Mn_3O_4.

CALCULATION.—$Mn \times 1.388 = Mn_3O_4$.

Total Sulfur.—Weigh 5–10 grams of the sample, prepared as previously directed to pass a 0.5-mm. sieve, into a 100-cc. nickel crucible; add an equal weight of anhydrous Na_2CO_3 and mix well with a stout nickel stirring rod of suitable length to permit introduction into the muffle to be used in the fusion. Pipette carefully 4 cc. of water into each 10 grams of soil and stir well to a stiff paste, adding more water if necessary, a few drops at a time. Add immediately successive portions of about 1 gram of Na_2O_2 (free from S), stirring well after each addition to prevent frothing over. Continue to add Na_2O_2 until the mixture becomes dry and granular, and then add as a surface coating sufficient Na_2O_2 to make a total of 25 grams for each 10 grams of soil. Place the mixture in an electric muffle maintained at a temperature of 400–500° C. for the first half hour; then raise the temperature rapidly to bright red heat (about 900° C.) and continue the fusion at this temperature for about 10 minutes.

Withdraw the crucible from the muffle, manipulate it rapidly so as to cause the melt to spread out in a thin film over the interior and chill rapidly by contact with a good conductor in a cool atmosphere. Place the chilled crucible sideways in a 600-cc. beaker and cover with water. Add about 5 cc. of 95% alcohol to decompose Na_2MnO_4. Cover the beaker with a watchglass,

place on a cold hot plate and bring to a boil. Continue brisk boiling until all the melt is disintegrated (usually about 30 minutes). When the suspension has assumed a flesh-colored, flocculent appearance, with no glassy green lumps in the interior of the crucible, remove the latter and the rod from the beaker and wash any flaky particles back into the beaker with the aid of a rubber policeman, rinsing several times with hot water. (If any small glassy particles still cling to the inside of the crucible, boil water in the crucible until they are disintegrated, and add to the main portion.) Filter immediately by suction through a 9-cm. Büchner funnel into a liter beaker placed under a bell jar. When no more of the liquid can be drawn through the filter, return the residue with the filter paper to the original beaker, washing any adhering particles carefully from the funnel. Add about 1 gram of Na_2CO_3, macerate with the stirring rod, add 75–100 cc. of water, and bring to a brisk boil while stirring vigorously. Again filter through a Büchner funnel, using suction until nearly dry, and wash with 25-cc. portions of hot water to a total volume of 500–700 cc., depending upon the amount of sample originally taken.

To the solution add from a burette, slowly and with constant stirring, sufficient conc. HCl to neutralize to methyl red indicator. Then add 0.5 cc. excess of HCl and evaporate to a volume of 400 cc. To the boiling solution add slowly 10 cc. of 5% $BaCl_2$ solution and let stand overnight. Filter through a weighed Gooch crucible with an asbestos mat, ignite in an electric muffle (or place the Gooch crucible in a porcelain crucible over a free flame), cool in a desiccator and weigh as $BaSO_4$. Calculate to percentage of total S or SO_3, as desired.

CALCULATION.—$BaSO_4 \times 0.1373 = S$.
$BaSO_4 \times 0.3430 = SO_3$.

NOTE.—For sulfur present as sulfates see under Alkali Salts below.

Potash and Soda.—Determine the K_2O in 1 gram of the finely ground soil by the J. Lawrence Smith procedure, as described on page 64.

Subtract from the weight of the mixed chlorides the equivalent amount of KCl and calculate the difference to Na_2O.

CALCULATIONS.—$K_2PtCl_6 \times 0.3067 = KCl$.
$NaCl \times 0.5303 = Na_2O$.

Alkali Salts.—To 100 grams of soil in a 500-cc. bottle, add 250 cc. of water. Stopper, shake thoroughly and let stand overnight. Filter through a Pasteur-Chamberland filter. Evaporate 50 cc. of the filtrate in a platinum dish on the steam bath to dryness. Ignite at a low red heat to drive off organic matter, cool in a desiccator and weigh for Total Soluble Salts. Then dissolve the residue in the platinum dish in 10–15 cc. of hot water, transfer to a 50-cc. volumetric flask, cool and dilute to the mark. Take 10 cc. for titration with 0.1 N $AgNO_3$ for chlorides and 10 cc. for titration with 0.1 N HCl and methyl orange for alkali. Calculate to percentages of NaCl and Na_2CO_3; subtract from the percentage of total soluble salts and report the difference as Sulfates.

NOTE.—When much gypsum is present, the solution of the salts in hot water must be filtered through a small filter, the gypsum weighed separately and subtracted from the total amount of sulfates.

Humus.*—Place 10 grams of the sample in a Gooch crucible, extract with 1% HCl until the filtrate gives no precipitate with NH_4OH and $(NH_4)_2C_2O_4$, and remove the acid by washing with water. Wash the contents of the crucible (including the asbestos mat) into a glass-stoppered cylinder with 500 cc. of 4% NH_4OH (containing 2% of NH_3), and let stand, with occasional shaking, for 24 hours. During this time have the cylinder inclined as much as possible without bringing the contents in contact with the stopper, thus allowing the soil to settle on the side of the cylinder and exposing a very large surface to the action of the NH_4OH. Then place the cylinder in a vertical position and let stand for 12 hours to allow the sediment to settle. Filter the supernatant liquid (the filtrate must be perfectly clear), evaporate an aliquot, dry at 100° C. and weigh. Finally, ignite the residue and again weigh. Calculate the humus from the difference in weights between the dried and the ignited residues.

Humus Nitrogen.*—Digest 10 grams of the soil with 2% HCl and wash as nearly free of acid as possible with water. Extract the humus, as above, with a 3% solution of NaOH and determine nitrogen in the extract in the usual way (p. 87).

* Not an Association of Official Agricultural Chemists method.

Calcium Carbonate Required.*—Place 100 grams of soil in a 400-cc., wide-mouthed bottle, add 250 cc. of normal KNO_3 solution, stopper and shake continuously for 3 hours in a shaking machine, or every 5 minutes by hand. Let stand overnight. Draw off 125 cc. of the clear supernatant liquid, boil 10 minutes to expel CO_2, cool and titrate with a standard NaOH solution of which 1 cc. is equivalent to 4 milligrams of $CaCO_3$, using phenolphthalein indicator. Each cc. of NaOH used is equivalent to 0.01% of $CaCO_3$ required by the soil.

NOTE.—The acids and acid salts of the soil are difficultly soluble in water, but by treating with a salt solution such as NaCl or KNO_3, a double decomposition takes place, rendering them soluble. An equilibrium is reached, however, before this reaction runs to an end, and if, after having drawn off 125 cc. to titrate, 125 cc. of fresh KNO_3 are added to the bottle and the bottle again shaken for 3 hours, 125 cc. drawn off will give a titration which is more than one-half of the first. By continuing this process until the last 125 cc. show practically no acidity, a series of titrations is obtained, the sum of which represents the total acidity of the 100 grams of soil. It has been found by working with a number of different soils that, as an average, the sum of such a series is 2.5 times the first titration. Consequently, when the NaOH is made up so that 1 cc. is equivalent to 4 mg. of $CaCO_3$ and 125 cc. (which represents 50 grams of soil) are titrated, each cc. required to neutralize corresponds to 0.01 gram of $CaCO_3$ required by the 100 grams of soil tested.

Reaction (Qualitative Test).—Place strips of neutral litmus paper in the bottom of several Petri dishes and lay over these 1 or 2 thicknesses of filter paper (free from acid). Place a portion of the sample on the filter paper. With a clean spatula press the soil down firmly against the paper and add sufficient freshly boiled and cooled water to saturate the soil. Cover the dish, let stand 30 minutes and note the color of the test paper.

NOTE.—The filter paper gives a uniform background and evenness of contact. A check Petri dish containing neutral litmus paper and filter paper moistened with the same water should be allowed to stand under the same conditions.

HYDROGEN-ION CONCENTRATION
(pH Value)

General.—The hydrogen-ion concentration (H^+) of liquids or dilute solutions is an expression of the intensity factor of acid or

*Not an Association of Official Agricultural Chemists method.

alkaline properties as opposed to the quantity factors "acidity" and "alkalinity." The latter are usually expressed in terms of normality. A 0.1 N solution of HCl has 10 times the "acidity" of a 0.01 N HCl solution, but there is substantially no difference in the hydrogen-ion concentration of the two solutions, *i.e.* the number of moles of ionized hydrogen per liter. Furthermore, since by the mass law the product of the hydrogen-ion concentration times the hydroxyl-ion concentration is a constant, the acid and alkaline intensities may both be expressed in terms of the hydrogen-ion concentration. On account of the very low numerical values encountered in hydrogen-ion concentration measurements it has been found convenient to express them in terms of pH values, which are derived from the relationship:

$$\text{pH} = \log \frac{1}{(\text{H}^+)}.$$

Table XXXII may be used for converting pH values into actual hydrogen-ion concentrations. Absolute "neutrality" at 22° C. corresponds to a pH value of 7.00.

General Methods.—Hydrogen-ion concentration may be determined electrometrically by means of the hydrogen electrode and the potentiometer, or colorimetrically. The colorimetric methods depend upon the use of indicators whose colors in solution are characteristic of the pH value of the solution. The most accurate results are obtained by the use of standard buffer solutions, which generally consist of mixtures of some acid and its alkali salts in varying but definite proportions, each mixture having a known pH value. For details of their preparation the literature on the subject should be consulted. (Certain prepared buffer standards may now be obtained from various chemical supply houses.) For most laboratory control work on solutions which are not too deeply colored or too turbid the Drop Ratio Method of pH value determination is the most convenient and is sufficiently accurate.

Drop Ratio Method.—Reagents.—(*a*) *Stock Solutions of Indicators.*—The indicators commonly used are those recommended by Clark and Lubs, as shown in Table XXXIII. This table gives the common names, the concentration most convenient for use, a rough indication of the color change and the useful pH range, and in the last column the amount of alkali required

TABLE XXXII*—HYDROGEN-ION CONCENTRATIONS AND CORRESPONDING pH VALUES

pH Value	H^+ Concentration
$n.00$	1.00×10^{-n}
$n.05$	$8.91\times10^{-(n+1)}$
$n.10$	7.94
$n.15$	7.07
$n.20$	6.31
$n.25$	5.62
$n.30$	5.01
$n.35$	4.46
$n.40$	3.98
$n.45$	3.54
$n.50$	3.16
$n.55$	2.82
$n.60$	2.51
$n.65$	2.24
$n.70$	1.99
$n.75$	1.78
$n.80$	1.58
$n.85$	1.41
$n.90$	1.26
$n.95$	1.12
$(n+1).00$	1.00

EXAMPLE: Find the H^+ concentration for pH 6.55.

$n=6$ and $n+1=7$.

H^+ concentration $=2.82\times10^{-7}$

$=0.000000282$.

to make a stock solution from 0.1 gram of the dye. To prepare the stock solutions, weigh out carefully 0.1 gram of the dry powder and grind in an agate mortar with the amount of 0.05 N NaOH solution shown in the last column of Table XXXIII. When solution is complete dilute to 25 cc. with distilled water and preserve in glass-stoppered bottles. These solutions keep well, with the exception of methyl red which is not very stable and is more conveniently prepared directly for the tests by dis-

* American Public Health Association: "Standard Methods of Water Analysis," 39 (1925).

solving 0.05 gram in 150 cc. of alcohol and diluting to 250 cc. with distilled water.

(*b*) *Test Solutions of Indicators.*—With phenol red and cresol red, dilute 1 cc. of the stock solution with 19 cc. of distilled water.

With thymol blue, brom thymol blue, brom phenol blue and brom cresol purple, dilute 1 cc. of the stock solution with 9 cc. of water.

With methyl red, dissolve 0.05 gram of the dry powder in 150 cc. of 95% alcohol and dilute to 250 cc. with water.

Place each test solution in a dropping bottle, properly labeled.

(*c*) *NaOH Solution.*—Approximately 0.05 N. Dissolve 2 grams of NaOH in water and dilute to 1 liter.

(*d*) *HCl Solution.*—Approximately 0.05 N. Dilute 4 cc. of conc. HCl to 1 liter with distilled water.

(*e*) *KH_2PO_4 Solution.*—Dissolve 2 grams of KH_2PO_4 in water and dilute to 100 cc.

TABLE XXXIII—CLARK AND LUBS' LIST OF INDICATORS

Chemical Name	Common Name	Concentration *Per Cent*	Color Change	pH Range	0.05 N NaOH per 0.1 Gram cc.
Thymol sulfon phthalein (acid range).	Thymol blue (see below)	0.04	Red-yellow	1.2–2.8	4.3
Tetra bromo phenol sulfon phthalein.....	Brom phenol blue	0.04	Yellow-blue	3.0–4.6	3.0
Ortho carboxy benzene azo dimethyl aniline.....	Methyl red	0.02	Red-yellow	4.4–6.0	7.4
Dibrom ortho cresol sulfon phthalein.	Brom cresol purple	0.04	Yellow-purple	5.2–6.8	3.7
Dibrom thymol sulfon phthalein.	Brom thymol blue	0.04	Yellow-blue	6.0–7.6	3.2
Phenol sulfon phthalein...	Phenol red	0.02	Yellow-red	6.8–8.4	5.7
Ortho cresol sulfon phthalein.....	Cresol red	0.02	Yellow-red	7.2–8.8	5.3
Thymol sulfon phthalein..	Thymol blue	0.04	Yellow-blue	8.0–9.6	4.3

APPARATUS.—(*a*) *Test-tubes.*—Select 22 or more test-tubes of uniform bore and as nearly colorless as possible. Mark each tube at the height corresponding to 10 cc. (The height of the marks should not vary more than 3 or 4 mm. for all the tubes.)

(*b*) *Comparator.*—Bore into the end of a suitable block of wood 9 holes in 3 parallel rows, making the holes of sufficient diameter and depth so that the test-tubes may be set into them

with the 10-cc. mark well below the surface (see Fig. 38). Holes 1–4–7 should be placed as close to one another as can be done without breaking through the intervening walls; and similarly with holes 2–5–8 and 3–6–9. From the front of the block, perpendicular to these holes and running through each of the series 1–4–7, 2–5–8 and 3–6–9, bore smaller holes through which the test-tubes may be viewed. Before use it is well to paint the whole block, especially the holes, a non-reflecting black.

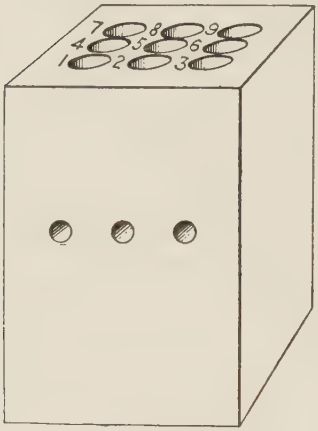


Fig. 38.—pH Value Comparator.

Procedure.—In each of 9 test-tubes, numbered 1 to 9 inclusive, place 1 drop of 0.05 N NaOH (2 drops in the case of thymol blue) and add 1, 2, 3, 4, etc., drops of the indicator to the respective tubes. In each of 9 other tubes, numbered 9 to 1 inclusive, place 1 drop of 0.05 N HCl* and add 9, 8, 7, 6, etc., drops of the indicator to the respective tubes. Fill each tube to the 10-cc. mark with distilled water and arrange them in pairs, each pair consisting of 1 alkaline and 1 acid tube which when taken together contain a total of 10 drops of indicator. In another test-tube place 10 drops of the indicator and sufficient of the liquid sample under examination to fill it up to the 10-cc. mark.

Place the tube containing the sample with the indicator added to it in hole 2 of the comparator. Back of it, in hole 5, place a test-tube containing 10 cc. of distilled water. In holes 1 and 4 place one of the pairs of the indicator tubes, for example alkaline tube 1 and acid tube 9; and in holes 3 and 6 place the next pair in the series, for example alkaline tube 2 and acid tube 8. Compare the colors of the indicator pairs with the sample by viewing the liquids horizontally. When a pair of tubes is found which matches the color of the sample, look up the corresponding pH value in Table XXXIV.

* In the case of brom phenol blue, use 1 cc. of 0.05 N HCl; and in the case of cresol red and thymol blue, use 1 drop of 2% KH_2PO_4 solution.

If the sample is colored or turbid, back up each pair of indicators with a third test-tube containing 10 cc. of the sample without indicator placed in the comparator holes 7 and 9. In this case a second tube of distilled water should be superimposed on the unknown tube by placing it in hole 8. The color comparisons are then made by looking through the 3 tubes in each case.

TABLE XXXIV—DROP RATIOS AND CORRESPONDING pH VALUES. (GILLESPIE)

Drops of Indicator in Each Pair		pH Values of Pairs with Various Indicators						
Alkaline Tube	Acid Tube	Brom Phenol Blue	Methyl Red	Brom Cresol Purple	Brom Thymol Blue	Phenol Red	Cresol Red	Thymol Blue
1	9	3.1	4.05	5.3	6.15	6.75	7.15	7.85
1.5	8.5	3.3	4.25	5.5	6.35	6.95	7.35	8.05
2	8	3.5	4.4	5.7	6.5	7.1	7.5	8.2
3	7	3.7	4.6	5.9	6.7	7.3	7.7	8.4
4	6	3.9	4.8	6.1	6.9	7.5	7.9	8.6
5	5	4.1	5.0	6.3	7.1	7.7	8.1	8.8
6	4	4.3	5.2	6.5	7.3	7.9	8.3	9.0
7	3	4.5	5.4	6.7	7.5	8.1	8.5	9.2
8	2	4.7	5.6	6.9	7.7	8.3	8.7	9.4
8.5	1.5	4.8	5.75	7.0	7.85	8.45	8.85	9.55
9	1	5.0	5.95	7.2	8.05	8.65	9.05	9.75

NOTES.—(1) The liquids should be between 25 and 30° C. when the comparisons are made. If necessary to work at other temperatures, it should be so stated in reporting.

(2) Under the most favorable conditions this method should yield results accurate to 0.2 of a pH number.

REFERENCES.—American Public Health Association: "Standard Methods of Water Analysis" (1925); W. M. Clark: "The Determination of Hydrogen Ions" (1920).

CHAPTER XII

MISCELLANEOUS ANALYSES

LEATHER

Preparation of Sample.—Reduce the sample for analysis to as fine a state of division as practicable, either by cutting, grinding or rasping. Avoid heating the sample.

Moisture.—Dry 10 grams for 16 hours between 95 and 100° C. Cool in a desiccator and keep the dish or weighing bottle tightly covered while weighing. Report the loss in weight as Moisture.

Fat and Oil.—Extract completely 5–10 grams of the air-dry sample in a Soxhlet apparatus with petroleum ether* boiling between 50 and 80° C. Evaporate off the ether and dry the extract at 100° C. to approximately constant weight, weighing at intervals of 1 hour.

Or, if preferred, extract 30 grams of leather as described above. In the latter case, the extracted leather, when freed of solvent, may be used for the determination of Water-soluble Material.

Total Ash.—Incinerate 10–15 grams in a tared dish at a dull red heat until carbon is consumed. If it is difficult to burn off all the carbon, treat the ash with hot water, filter through an ashless filter and ignite the filter and residue in the dish. Then add the filtrate, evaporate to dryness and ignite. Cool in a desiccator and weigh the mineral matter.

Water-insoluble Ash.—Dry a portion of the leather after it has been extracted with water as below described and determine the ash as in the previous paragraph. Calculate to percentage of the original leather.

CALCULATION.—

Let A = weight of ash obtained, in grams;

M = moisture in original leather, expressed as a decimal;

* The extraction will require 8–12 hours, depending upon the amount of fat. If convenient, let the extraction run overnight. Place a layer of fat-free cotton above and below the ground leather in the extractor.

F = fat in original leather, expressed as a decimal;
G = grams of water-extracted leather taken; and
P = percentage of water-insoluble ash in original leather.

Then $$P = 100A\left(\frac{1-M-F}{G}\right).$$

Water-soluble Material.—Weigh 30 grams of the finely divided sample. If the fat content as previously determined is over 6%, extract the 30-gram charge with petroleum ether distilling between 50 and 80° C. and let the ether evaporate spontaneously from the leather before proceeding with the water extraction (see under Fat and Oil above). To the charge add sufficient water to cover and thoroughly soak it, and mix well. Let stand overnight. Transfer the leather and extract to a percolator which may be kept at 50° C. (The Reed-Churchill Extractor is recommended.) Percolate with water at 50° C., collecting approximately 2 liters of percolate in 3 hours. Cool to room temperature, dilute to exactly 2 liters and mix thoroughly.* Pipette 100 cc. of the extract into a weighed flat-bottomed dish 2.75–3 inches in diameter. Evaporate to dryness and dry to constant weight at 100–105° C. From this weight calculate the percentage of Water-soluble Matter.

Glucose.—Place 200 cc. of the water extract prepared above in a 500-cc. flask, add 25 cc. of a saturated solution of normal lead acetate; shake frequently for 5–10 minutes, and filter through a dry filter. Keep funnels and beakers covered to prevent evaporation. Add to the filtrate an excess of solid $K_2C_2O_4$. Mix frequently for 15 minutes and filter, returning the filtrate until it runs through clear. Pipette 150 cc. of this clear filtrate into a 500-cc. Erlenmeyer flask. Add 5 cc. of conc. HCl and boil under a reflux condenser for 2 hours. Cool, add a small piece of litmus paper and neutralize with anhydrous Na_2CO_3. Transfer to a 200-cc. volumetric flask and dilute to volume. Filter through a dry double filter, rejecting the first filtrate. The final filtrate must be clear. Determine the dextrose immediately in 50 cc. of this solution, using the Munson and Walker method as described under Total Reducing Sugars (p. 551). Calculate the results to

* If necessary to keep the solution for any length of time, add a few drops of toluene to prevent fermentation.

percentage of the original leather and report as Glucose, Calculated as Dextrose.

In making the determination place 25 cc. of the $CuSO_4$ solution and 25 cc. of the alkaline tartrate solution in a 400-cc. beaker. Add 50 cc. of the prepared leather solution, heat to boiling in exactly 4 minutes, and boil for 2 minutes. The burner should be adjusted by a preliminary trial so that these conditions are fulfilled. Filter immediately without diluting through a weighed Gooch crucible containing an asbestos mat. Wash thoroughly with hot water, then with alcohol, and finally with ether. Dry for $\frac{1}{2}$ hour at the temperature of boiling water and weigh as Cu_2O.

NOTE.—If the above conditions of dilution, etc., are all fulfilled, 50 cc. of the clarified and neutralized solution will correspond to 0.5 gram of the original leather (assuming exactly 30 grams taken for the water-soluble determination).

Nitrogen.—Determine N on 1.5 grams of the leather by the Gunning modification of the Kjeldahl method, as described on page 87. Multiply the nitrogen by 5.62 to obtain the amount of Hide Substance.

Chromium in Chrome Leather.—For this determination see page 749.

Free Mineral Acid.—Most leathers when moistened are acid to litmus but this, unless extremely marked, is no evidence of free mineral acid. A marked acid reaction, however, especially in the presence of much sulfate, is suspicious. On the other hand, even if the leather contains free H_2SO_4, the ash will usually be alkaline, since acid is driven off on ignition and a portion of the sulfates is reduced to sulfides, and even to carbonates or free bases, especially in the case of lime salts. There is no method which will give with certainty a true figure for free H_2SO_4. The 2 methods which are probably the best are described below:

(1) JEAN METHOD.—Dry 10 grams or more of finely divided leather at not over 95° C. (drying in a vacuum desiccator is preferable) and extract with *absolute* alcohol in a Soxhlet extractor, placing about 0.5 gram of Na_2CO_3 powder in the flask to combine with any acid dissolved by the alcohol. Extract until the alcohol comes over colorless. Distill off the alcohol, transfer to a platinum dish and ignite to a char. Leach out with hot water, filter,

and determine the total SO_3 in the solution by acidifying first with HCl and then adding to the boiling solution an excess of $BaCl_2$ solution. Filter, ignite and weigh the $BaSO_4$ in the usual way. Calculate to H_2SO_4.

CALCULATION.—$BaSO_4 \times 0.4202 = H_2SO_4$.

NOTE.—The alcohol used must be absolute and freshly prepared by distilling from quicklime. The method is based on the fact that H_2SO_4 is soluble in absolute alcohol, but sulfates are not. For this reason also the leather must be dried, but extreme drying, and especially the use of a high temperature, must be avoided, as this will cause the acid to attack and combine with organic constituents of the leather.

If the above conditions are complied with, a positive result may be taken as proof of the presence of free acid; but a negative result is not conclusive evidence that acid is not present, even in injurious quantities, since it has been proved that even a long extraction may fail to remove all the acid from the leather.

(2) PROCTOR AND SEARLE METHOD.—Moisten 2–3 grams of the leather in a platinum dish with exactly 40 cc. of accurately standardized 0.1 N Na_2CO_3 solution; evaporate to dryness and char at a dull red heat, preferably in a muffle, until most of the carbon has been removed. This drives off practically all organic sulfur, while the reduction of sulfates is very slight. Pulverize the carbonaceous mass with a glass rod and leach with boiling water, filtering through a small quantitative filter paper. Dry the filter paper, return it to the mass in the dish, and ignite the whole until all carbon has disappeared. Cool and add to the residue from a burette an amount of 0.1 N HCl or H_2SO_4 exactly equivalent to the Na_2CO_3 originally added. Cover the dish and heat on the steam bath for 30 minutes. Filter, if necessary, into the flask containing the first filtrate, washing the paper thoroughly with water until free from acid. Cool the solution and add 2 or 3 drops of methyl orange indicator. If the solution is alkaline, report the acidity as none; if acid, titrate to a distinct yellow color with the 0.1 N Na_2CO_3 and express the result as percentage of free H_2SO_4. With each set of determinations run a blank through the entire process, using the standard solutions. If the blank is over 0.3 cc., repeat the determination.

CALCULATION.—1 cc. 0.1 N $Na_2CO_3 = 0.0049$ gram H_2SO_4.

NOTE.—The two above methods for free acid are chiefly of value in comparing different leathers, although if carefully carried out they give results

which are reasonably accurate. The Proctor and Searle method can be used only on vegetable tanned leathers. It gives results much too high on alum or chrome tanned leathers. Probably the most accurate method at present known is that of Wuensch, but it is a troublesome and time-consuming procedure. It is described in H. R. Proctor: "Leather Industries Laboratory Book of Analytical and Experimental Methods," 371 (1908).

Combined Tannin.—Deduct from 100% the sum of the percentages of moisture, fat and oil, water-insoluble ash, water-soluble material, and hide substance (see under Nitrogen). The remainder is the percentage of combined tannin.

REFERENCE.—The above procedures, with the exception of the Jean method for free mineral acid, are essentially the methods of the American Leather Chemists' Association.

CHROMIUM IN CHROME SALTS AND LEATHERS

General.—The most accurate method for the determination of chromium in chrome salts is to oxidize to the chromate condition and then determine the latter either gravimetrically, by precipitation as $PbCrO_4$, or volumetrically.

Chrome Liquors (Chrome Tanning Liquors, Chromium Acetate, etc.).—(*a*) ONE BATH CHROME LIQUORS (USED IN TANNING).*—Dilute a weighed quantity of the liquor with water to a definite volume, so that the dilution contains from 0.15 to 0.25% of Cr_2O_3. Pipette 10 cc. of this solution into a 300-cc. Erlenmeyer flask and add about 50 cc. of water and 2 grams of Na_2O_2. Boil gently for 30 minutes, adding water if necessary to keep the volume from falling below about 15 cc. Cool, neutralize with conc. HCl and add 5 cc. excess. Again cool and add 10 cc. of 10% KI solution. After 1 minute run in from a burette 0.1 N thiosulfate solution until the iodine color nearly disappears, then add a few cc. of starch solution and titrate to the disappearance of the blue. Calculate to Cr_2O_3.

CALCULATION.—1 cc. 0.1 N thiosulfate = 0.002534 gram Cr_2O_3.

(*b*) CHROMIUM ACETATE SOLUTIONS (USED IN MORDANTING).—Weigh out about 10 cc. accurately and dilute to 100 cc. in a volumetric flask. Mix thoroughly and pipette 10 cc. into a 300-cc. Erlenmeyer flask. Then proceed as above.

* *J. Am. Leather Chem. Assoc.*, **14**, 667 (1919).

(*c*) Gravimetric Method.—If the material is free from sulfates, the Cr_2O_3 may be determined gravimetrically as follows:

Oxidize with peroxide as above. Filter out any insoluble matter. Heat nearly but not quite to boiling. Make acid with acetic acid and add an excess of lead acetate solution containing a few drops of acetic acid. Let stand on the steam bath until clear, but avoid long standing on account of the danger of forming basic compounds. Filter through a weighed Gooch crucible, wash with hot water, and dry at 105° C. Set the Gooch crucible inside of a larger platinum crucible, ignite to very dull redness, cool and weigh as $PbCrO_4$. Calculate to Cr_2O_3.

Calculation.—$PbCrO_4 \times 0.2352 = Cr_2O_3$.

Note.—In the case of chrome liquors containing impurities such as organic matter, dyestuffs, etc., oxidation cannot be effected with peroxide alone. The solution must be rendered alkaline with NaOH and boiled with conc $KMnO_4$ solution. The violet color of the permanganate disappears on boiling and more permanganate must be added and the solution again boiled. Repeat this process until a violet-red color finally persists even after boiling and then remove the small excess of $KMnO_4$ by warming the solution with 2 drops of alcohol. Filter and wash and determine the Cr_2O_3 in the filtrate.

Chromium in Chrome Leather.*—Ash 3 grams of leather. Mix the ash thoroughly with 4 grams of a mixture of equal parts of Na_2CO_3, K_2CO_3 and powdered borax glass and fuse in a platinum crucible for 30 minutes. Dissolve the cooled fusion in hot water and slightly acidify with HCl. Filter. If there is any residue on the filter, ash it and treat the ash with 1 gram of the above fusion mixture in the same manner as the original ash, adding the solution to the first. Make up to 500 cc., and pipette out 100 cc. of this solution into an Erlenmeyer flask. Neutralize with conc. HCl, add 5 cc. in excess and then add 10 cc. of 10% KI solution and titrate as previously described.

SUMAC EXTRACT

Solutions Required.—(1) *Potassium Permanganate.*—0.50 gram of pure $KMnO_4$ per liter. Standardize accurately (see page 9).†

(2) *Indigo Carmine.*—5 grams of pure indigo carmine and 50 grams of conc. H_2SO_4 per liter. This must be filtered and should

* *J. Am. Leather Chem. Assoc.*, **14**, 668 (1919).

† The normality of this solution is approximately 0.016.

give a pure yellow, free from any trace of brown, when oxidized with $KMnO_4$. 25 cc. of this solution should equal about 30 cc. of the $KMnO_4$ solution and, if necessary, must be diluted to that strength.

NOTE.—Indigo carmine is potassium or sodium sulfindigotate. As it is frequently difficult to obtain it of satisfactory purity, the solution may be made up from synthetic indigo as follows: Dissolve 1 gram of "indigo pure" by heating to 75–80° C. with 25 cc. of conc. H_2SO_4 for 1 hour, stirring occasionally with a glass rod. After cooling, add 25 cc. more of conc. H_2SO_4, transfer to a liter volumetric flask and dilute to the mark.

(3) *Gelatin Solution.*—Soak 20 grams of Nelson's gelatin in water for 2 or 3 hours. Then dissolve on the steam bath with the addition of more water and dilute to 1 liter.

(4) *Saturated NaCl Acid Solution.*—Make up a 5% solution of H_2SO_4 and saturate with common salt.

Standardization.—Dilute 25 cc. of the indigo-carmine solution in a large, white porcelain dish with about 750 cc. of tap water and add the $KMnO_4$ drop by drop from a burette until a pure yellow is obtained, stirring the liquid constantly. The dropping should be as nearly as possible at a similar rate for each experiment and should be slower toward the end of the titration. The final end-point must be approached cautiously by adding the $KMnO_4$ very slowly until the pure yellow liquid shows a faint pinkish rim, which can most clearly be seen on the shaded side. At least 2 titrations should be made.

Total Astringency.—Weigh out 2.5–3.5 grams of the sumac extract and dilute to 500 cc. Place 5 cc. of this solution in a large porcelain dish with 25 cc. of the indigo-carmine solution and 750 cc. of tap water. Titrate with the $KMnO_4$ solution as above described, running at least 2 determinations. Subtract from this titration the amount of $KMnO_4$ required by the indigo solution in standardizing, and from the known strength of the $KMnO_4$ solution calculate the number of cc. of 0.01 N $KMnO_4$ reduced by the total astringency. From this calculate the total astringency as tannins.

CALCULATION.—1 cc. 0.01 N $KMnO_4 = 0.0004157$ gram tannin.

Astringent Non-tannins.—To 50 cc. of the dilute sumac solution above referred to add 25 cc. of the gelatin solution, 25 cc. of the acid salt solution and 10 grams of china clay or

kaolin. Shake thoroughly for about 5 minutes and filter through a dry filter. This removes the tannins. Titrate 10 cc. of the filtrate (corresponding to 5 cc. of the original sumac extract solution) for non-tannins in exactly the same manner as the total astringency was determined, and calculate the percentage of non-tannins by means of the same factor.

Tannin.—Subtract the percentage of non-tannins from the percentage of total astringency and report the difference as the percentage of Tannin in the extract.

REFERENCES.—H. R. Proctor: "Leather Industries Laboratory Book of Analytical and Experimental Methods," 2d ed., 227; Leach: "Food Inspection and Analysis," 4th ed., 429; Knecht-Rawson-Loewenthal: "Manual of Dyeing," 2nd ed., **2,** 802.

20 PER CENT PARA RUBBER COMPOUND

General.—This method is the procedure recommended by the Underwriters' Laboratories for Code Rubber and should be used for all rubber insulation on wires and cables other than 30% Para Compound. All determinations should be performed in duplicate and must check within 0.2%, calculated on the total sample. The average value should be taken as the true value.

Preparation of Sample.—Take a sufficient length of wire to give at least 15 grams of rubber compound. Remove the outer coverings and sandpaper the surface of the rubber sufficiently to remove all irregularities, and in any case to a depth of not less than 0.003 inch. (This is to get rid of extraneous matter absorbed from the impregnating compound.) Wipe with a dry cloth.

In some cases after the mechanical cleaning it may be necessary to clean further with a cloth dampened with ether, taking care to avoid allowing the ether to penetrate the compound to any marked extent. Strip all the rubber from the wire and cut into small pieces. Grind this entire sample in a mill until it is finely divided, avoiding heating. Spread the sample out on a piece of glazed paper, pass over it a strong magnet to remove any metal which may have come from the grinder, and then mix thoroughly.

Acetone Extract.—Extract a 2-gram sample with pure acetone until the sample is practically free from matter soluble in acetone

(not less than 5 hours), the speed of condensation being such that at least 150 drops per minute fall directly upon the sample. Distill off the acetone, dry the flask with the extract to constant weight at 95–100° C., and weigh.

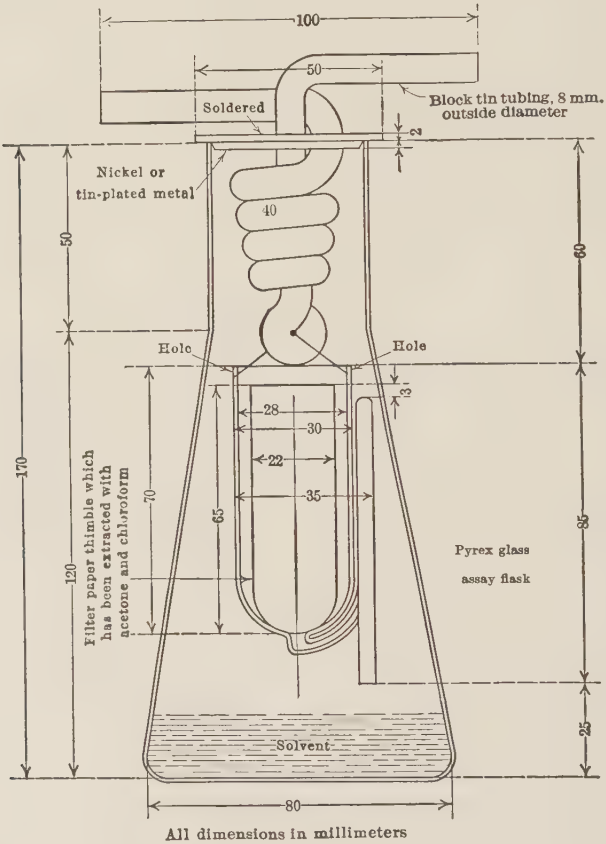


FIG. 39.—Extraction Apparatus for Rubber.

Extraction Apparatus.—A very satisfactory extractor is that recommended by the Joint Rubber Insulation Committee and shown in Fig. 39, but any extractor may be used which conforms to the following specifications:

1. The extraction cup shall be surrounded by the vapor of the solvent at its boiling point.

2. The condensed solvent shall fall directly on the sample.

3. The outlet from the extraction cup shall be at the bottom only.

4. No rubber or cork stoppers shall come in contact with the solvent.

5. The sample shall be put directly into the extraction cup without the use of a paper thimble, a disk of filter paper or its equivalent at the bottom of the cup being depended upon to hold back the solid particles.

Chloroform Extract.—Without drying the residue from the acetone extraction, extract with $CHCl_3$ for 3 hours. If at this time the solution is not coming through colorless, continue until it is colorless, provided the total extraction does not exceed 5 hours. Distill off the $CHCl_3$, dry the flask with the extract to constant weight at 95–100° C., and weigh.

Alcoholic Potash Extract.—Prepare a normal alcoholic KOH solution* by dissolving pure KOH in 95% alcohol which has been freshly distilled over KOH. Let the solution stand overnight and filter.

Dry the residue from the $CHCl_3$ extraction at 50–60° C., place in a 200-cc. Erlenmeyer flask and boil with a reflux condenser for 4 hours with 50 cc. of normal alcoholic KOH. Filter the solution into a beaker; wash first with 100 cc. of absolute alcohol, then with 50 cc. of hot water, and evaporate to approximate dryness. Add a little water, transfer into a separatory funnel, dilute to 100 cc. and acidify with dil. HCl. Shake out with 20-cc. portions of ether until the last portion is colorless, after which shake out twice more. Shake out the ether solution twice with 50 cc. of water. Filter the ether solution into a small weighed beaker and wash the filter with a little ether; evaporate off the ether without boiling, dry to constant weight at 95–100° C., and weigh.

Total Sulfur.—Mix 0.5 gram of the sample with 4 grams of Na_2O_2 (sulfur free) and 6 grams of K_2CO_3 in a dry 15-cc. iron crucible; cover the crucible, insert into a close-fitting hole in an asbestos board and place about 10 cm. above a flame turned very low. Gradually increase the flame until the mixture fuses, proceeding cautiously, as rapid heating will cause an explosion; and then apply the full heat for 15–20 minutes. Rotate the crucible

* 56.1 grams of KOH per liter.

while the melt solidifies. When cool place the crucible and cover in a 200-cc. casserole filled with water, add 5–10 cc. of bromine water, and boil until the melt is dissolved and the bromine expelled. Let the precipitate settle, with the addition of MgO if necessary; decant the liquid through a thick filter and wash the residue by decantation with hot water until practically neutral. Acidify the filtrate with HCl, evaporate to dryness and dehydrate the silica; take up in 400 cc. of water, add 5 cc. of dil. HCl and filter. Bring to a boil and add slowly a slight excess of hot 10% $BaCl_2$ solution. Let stand overnight, filter, wash, ignite and weigh the $BaSO_4$. Calculate to S.

CALCULATION.—$BaSO_4 \times 0.1373 = S$.

NOTE.—In case of disagreement on total sulfur, the Carius' Method shall be used. (See Gattermann: "Practical Methods of Organic Chemistry.")

Ash.—Place in a small porcelain dish a weight of acetone-extracted compound which, before such extraction, had a weight of 1 gram. Burn off the rubber completely at as low a temperature as possible, without letting it catch fire. (High temperatures must be carefully avoided.) This may be done in either of 2 ways: First, by inserting the dish into a close-fitting hole in an asbestos board and heating carefully over a small flame, the dish afterwards being placed on a triangle and just sufficient flame applied to the sides to remove any condensation; or, second and preferably, by placing the dish containing the sample near the mouth of a suitably heated muffle furnace. Cool in a desiccator and weigh the ash.

Free Sulfur.—The free S will be in the acetone extract. Add to the flask containing the acetone extract 10–15 cc. of fuming HNO_3. Place the flask on the water bath until all is in solution. Transfer to a hot plate and add small portions of $KClO_3$ until the solution is decolorized. Evaporate to dryness, carefully avoiding any SO_3 fumes which would be absorbed by the solution. Take up the residue with 50 cc. of water, add 3 cc. of conc. HCl and filter into a 600-cc. beaker. Dilute to about 400 cc., heat to boiling and precipitate with $BaCl_2$ in the usual manner. Let stand overnight, protected from SO_3 fumes. Filter off the $BaSO_4$. Ignite, cool in a desiccator and weigh. Calculate to S. Subtract from this result any S found in a blank determination which should be carried through simultaneously.

NOTE.—The procedure for free sulfur is not included in the Underwriters' methods.

CASE-HARDENING COMPOUNDS

General.—For case-hardening steel a great variety of substances is used. Among the more common ones are materials containing coke, charcoal, flour, grain, fibers, $BaCO_3$, cyanides, Na_2CO_3, crushed bone, powdered glass, rosin, gums, etc. The sample should first be examined under the microscope to note its general appearance and to detect, if possible, any of the foregoing substances.

The following is an attempt at a general scheme of analysis but may have to be modified to suit conditions.

Ether Extract.—Mix the sample thoroughly and quarter it down to about 50 grams. Extract 10 grams or more with ether in a Soxhlet extraction thimble, collecting the extract in a weighed Soxhlet flask. Evaporate off the ether, dry the residue at 100° C., and weigh. If the extract is appreciable in amount, it should be tested for rosin and its identity ascertained, if possible, by determining the saponification number, iodine number, refractive index, etc.

Moisture.—Dry 2 grams at 100° C. until the weight is constant. Report the loss as Moisture.

If the sample contains much oil, dry the residue from the ether extraction at 100° C. The moisture is the original weight taken, minus the final dry weight, minus the weight of ether extract.

Volatile Matter.—The volatile matter is determined in exactly the same manner as the volatile matter in the Proximate Analysis of Coal (p. 214). Grind 2 grams of the material, on which the moisture has been determined, rapidly to a fine powder and place 1 gram in a covered platinum crucible over a Chaddock burner, gas pressure 1.1 inches, and burn for exactly 7 minutes. Cool and weigh. The loss is the volatile matter.

Ash.—Ignite 2 grams in a porcelain crucible until the ash is free from carbonaceous matter. Dry in a desiccator and weigh.

Loss on Heating at 850° C. for 6 Hours.—This should be done in a porcelain dish, 3 inches in diameter and 2 inches deep. Weigh the dish empty and then fill it with the compound, heaping it up and packing down. Weigh again to determine the amount of substance taken. Place in a muffle, the temperature of which

has been ascertained by means of a pyrometer, and heat at 850° C. for 6 hours. Cool in a desiccator and determine the loss in weight.

Analysis of Ash.—Analyze the ash in the ordinary manner for Ba (probably present as carbonate if at all), CaO, P_2O_5, SO_4, Na and K. Note whether the ash is alkaline or acid and, if so, determine the amount by titration. The presence or absence of carbonates should also be noted. If $Ca_3(PO_4)_2$ is found, the material probably contains ground bone.

Water Extract.—Extract 10–20 grams or more with hot water (after extracting with ether, if any oil is present) in a Soxhlet extractor, collecting the extract in a weighed flask. Evaporate off the water; dry at 100° C. and weigh. If the water extract is appreciable it should be analyzed. The best procedure is to dilute it to a given volume and ascertain its nature qualitatively and then make quantitative determinations on separate aliquots. It should be remembered that it is unnecessary to test for anything that is insoluble in water.

Nitrogen.—(*a*) Total Nitrogen.—This is determined by the Kjeldahl method, modified to include nitrogen present as nitrates, using 1–4 grams of the material (see p. 90).

(*b*) Nitrogen as Ammonia.—Place 1–5 grams in a 500-cc. round-bottomed flask. Add about 200 cc. of water and 5–10 grams of MgO, free from carbonates. Connect with a condenser and distill into 50 cc. of 0.1 N HCl. Titrate the excess of HCl with 0.1 N NaOH and calculate the difference to NH_3.

(*c*) Protein Nitrogen and Nitrates.—A qualitative test on the water extract will show whether or not nitrates are present. If they are not present, the difference between the total N and the N present as NH_3, will give the N present as protein, and this figure multiplied by 6.25 will give the amount of protein (see note).

If nitrates are present it is generally sufficient to report the difference between the total nitrogen and the ammoniacal nitrogen as Protein and Nitrate Nitrogen. The microscopical examination and the odor on burning will generally give indications as to whether protein is present or not.

(*d*) Nitrogen as Cyanide.—Cyanide may be detected qualitatively by acidifying the original material and *very cautiously*

noting the odor. If cyanide is present, digest 10 grams of the original material with warm water and wash by decantation once or twice, pouring the liquid through a filter. Finally transfer the material to a filter and wash thoroughly with warm water. Cool to room temperature and determine cyanogen by titrating with **0.1 N** $AgNO_3$, as described on page 47.

NOTE.—If cyanide is present, the total N as previously determined will include the N of the cyanide.

Carbide.—The presence of calcium carbide may be qualitatively detected by the odor of acetylene when the material comes in contact with water. An approximately quantitative estimation may be obtained by collecting the acetylene from a weighed amount of the sample under water in a nitrometer tube. 1 cc. of C_2H_2 at 0° C. and 760-mm. pressure is equivalent to 0.002866 gram of CaC_2.

Sulfide.—This may be detected by the odor of H_2S when the material is acidified with HCl, or in small amounts by the blackening of filter paper moistened with lead acetate solution.

The previous examination of the sample will generally give indications as to the nature of the sulfide. The amount of sulfur present as sulfide may be determined by treating 2 grams of the material with dil. HCl and bromine water, filtering, and determining the total sulfate in the filtrate by means of $BaCl_2$. On a separate portion determine the sulfur present as sulfate. The difference between these two determinations shows the amount of sulfur present as sulfide.

CUTTING COMPOUNDS

General.—These materials usually consist of a mixture of some fatty oil with a mineral oil, emulsified by means of soap and, as a rule, contain 40–60% of water. The soap is often, though not always, a potash soap. Whale oil and lard oil are the fatty oils generally used.

Moisture.—Dry approximately 5 grams in a flat platinum dish at 105° C. to constant weight. The loss represents moisture and volatile matter.

The moisture may also be determined by the Xylol Method (see p. 358).

Ash.—Ignite the residue from the moisture determination until the ash is white or light gray in color. Cool in a desiccator and weigh.

Soap.—Titrate the ash with 0.1 N HCl and methyl orange. Test the HCl solution with a platinum wire in a flame to see whether the base is Na or K. Calculate the titration to the proper soap.

CALCULATION.—1 cc. 0.1 N HCl = 0.0304 gram Na soap.
= 0.0320 gram K soap.

NOTE.—As a check, the titration should also be calculated to sodium or potassium carbonate and the weight thus calculated should agree approximately with the weight of the ash.

CALCULATION.—1 cc. 0.1 N HCl = 0.00530 gram Na_2CO_3.
= 0.00691 gram K_2CO_3.

Total Oily Matter.—Weigh out about 10 grams into a 200-cc. beaker, add 100 cc. of water, warm on the steam bath and add an excess of dil. H_2SO_4. Cool the mixture and transfer to a separatory funnel. Wash the beaker finally with $CHCl_3$ and add the washings to the separatory funnel. Shake out 3 times with portions of about 30 cc. of $CHCl_3$. After each treatment allow the 2 liquids to separate completely and clearly and then draw off the $CHCl_3$ extract into a weighed Soxhlet flask. Evaporate the $CHCl_3$ from the combined extracts in the Soxhlet flask, dry to constant weight at 105° C. and weigh the total oily matter.

Unsaponifiable Oil.—Weigh approximately 10 grams into a 300-cc. Erlenmeyer flask and add 50 cc. of 0.5 N alcoholic KOH. Saponify for 2 hours, or longer, over a low flame, using a reflux condenser. Add a few drops of phenolphthalein solution. If the mixture in the flask is not still alkaline, add 25 cc. more of alcoholic KOH and saponify for another 2 hours. The mixture should be alkaline after the saponification is complete. Add about an equal volume of water, connect the flask with an ordinary Liebig condenser and distill off at least $\frac{1}{2}$ of the liquid. Cool the residue, transfer to a large separatory funnel and dilute with several times its volume of cold water. Extract the solution 4 times with portions of about 50 cc. of ether. If the mixture is violently shaken it is likely to form an emulsion which can be broken up only with difficulty. Therefore mix the two by giving a rotating motion to the funnel or by laying it on its side and rolling

it. Draw off the lower layer each time into a second separatory funnel and wash the ether extract once with water. Pour the combined extracts into a weighed Soxhlet flask, evaporate off the ether and weigh.

NOTE.—Instead of ordinary ether, petroleum ether may be used. This is less likely to form emulsions, but care should be taken to use material which leaves no residue on evaporation at 100° C.

Uncombined Fatty Oil.—This is obtained by calculation. Calculate the amount of fat in the soap present by using the following factors:

$$\text{Combined Fat} = \text{Na Soap} \times 0.93.$$
$$= \text{K Soap} \times 0.88.$$

Add together the unsaponifiable oil and the fatty oil combined as soap and subtract the sum from the total oily matter. The difference represents the uncombined fatty oil.

Free Fatty Acid.—Weigh 20 grams into a 300-cc. Erlenmeyer flask, add 100 cc. of alcohol which has previously been warmed and made neutral to phenolphthalein with 0.1 N NaOH. Warm the mixture on the steam bath for about $\frac{1}{2}$ hour, titrate with 0.1 N NaOH and phenolphthalein to a permanent pink color and calculate the titration to oleic acid.

CALCULATION.—1 cc. 0.1 N NaOH = 0.0282 gram oleic acid.

METAL POLISHES

General.—Liquid metal polishes may be divided into 2 general classes: (1) Naphtha Polishes; (2) Fireproof Polishes.

The former consist essentially of naphtha containing an abrasive powder held in suspension by means of soap, with the odor of the naphtha usually covered up to some extent by an essential oil such as citronella or nitrobenzol. The second class is for the most part water emulsions of various solvents holding an abrasive powder in suspension. Carbon tetrachloride has been used to some extent either alone or in combination with naphtha. An examination of a metal polish should in general include a determination of the amount and character of the solvents, the soap and the abrasive.

Solvents.—Weigh out 100 grams of polish into a 250-cc. distilling flask provided with a thermometer and connected with a long condenser. Start the distillation in a water bath, *taking care that the flame is amply protected from any uncondensed vapors which may issue from the end of the condenser,* and collect the distillate in a 25-cc. weighed cylinder. When active distillation ceases, or if none takes place, substitute an oil bath for the water bath and continue the distillation up to 250° C., collecting the distillate in weighed cylinders, as before. The following fractions should be taken: (1) below 100° C.; (2) 100°–150° C.; (3) 150°–200° C.; (4) 200°–250° C.

The boiling points, odors, refractive indices and specific gravities of the various fractions will give indications of the character of the solvents. Those which are likely to be present are: turpentine, pine oil, rosin spirit, rosin oil, naphtha, kerosene, carbon tetrachloride, alcohol and water. The approximate "constants" of these solvents are given below:

	Specific Gravity at 15.5° C.	Distilling Temperature, °C.	Refractive Index
American turpentine	0.860–0.870	155–170	1.468–1.473 at 20° C.
Wood turpentine	0.855–0.910	159–165	1.468–1.475 at 20° C.
Pine oil	0.935–0.947	190–220	1.484–1.486 at 15.5° C.
Rosin spirit	0.856–0.880	Gradual rise (about 50% below 120°)	.....
Rosin oil	0.96–1.10	300–360	.....
Naphtha	0.700–0.750	50–150	.....
Kerosene	0.775–0.800	150–300	.....
CCl_4	1.60	77	.....
Alcohol, wood	About 0.800	About 65	.....
Alcohol, denatured	About 0.816	About 78	

Notes.—(1) Water will separate all other constituents except alcohol. If both water and alcohol are present the amounts can be roughly approximated by taking the volume and sp. gr. of the aqueous distillate and calculating from the sp. gr. tables for alcohol.

(2) If water is present, the distilling temperatures will be no indication of the boiling points of the other substances present. In such cases pour all the fractions which contain any water into a small separatory funnel, draw

off the water carefully, combine the residue with the remainder of the distillate and redistill from a small flask.

Soap.—Dry 15 grams of the polish on a Hofmeister schälchen, crush and extract the residue with ether in a Soxhlet extractor. After the ether-soluble materials are removed, extract the soap with alcohol (95%). Evaporate off the alcohol, dry at 105° C., and weigh. Examine the soap to determine whether it is a sodium, potassium, or ammonium soap.

In case no alcohol-soluble soap is obtained, it is probable that a lime soap is present, in which case the contents of the capsule should be acidified with 1 cc. of conc. HCl and extracted with ether. Evaporate off the ether, weigh the liberated fatty acids and calculate them as calcium oleate.

CALCULATION.—Fatty acids $\times 1.07$ = calcium oleate.

Boil the acidified contents of the capsule with hot water, filter, and make a qualitative test for Ca.

Free Ammonia.—If an ammonium soap is present or the polish smells of NH_3, weigh out 2–5 grams of the original polish into a flask, add 200 cc. of water and distill into 0.1 N acid. A spray trap should be used and a few drops of methyl red added to the acid. Titrate the excess acid with 0.1 N NaOH.

CALCULATION.—1 cc. 0.1 N acid = 0.0017 gram NH_3.

Combined Ammonia.—Dilute the solution remaining in the flask with 200 cc. of water, add 10 cc. of conc. NaOH, and distill as before. Calculate to NH_4 soap.

CALCULATION.—1 cc. 0.1 N acid = 0.03 gram NH_4 soap.

Abrasive.—Weigh out 10 grams of the metal polish, evaporate to dryness, taking proper precautions if the solvent is inflammable, ignite at a low red heat to burn off any organic matter, and weigh. Correct the ash thus formed for the ash of the soap, unless an NH_4 soap is present. Examine the ash microscopically to ascertain if it consists of tripoli or ground rock. If the latter, a qualitative analysis may be made, although the physical condition of the abrasive is of more importance than its chemical composition.

NOTE.—It should be remembered that all of the determinations are more or less approximate, due to various causes, and consequently calculations should be made to the nearest even percentage, except for the NH_3 determinations.

SOLDERING PASTE

General.—Soldering pastes generally consist of a mixture of $ZnCl_2$ and NH_4Cl with petrolatum. While they vary somewhat in composition their proportions are generally within the following limits:

$ZnCl_2$	15–20%
NH_4Cl	1– 5%
Water	Less than 5%

Since the salts are likely to settle out on standing, especially if the paste has been in a warm place, it is necessary before starting the analysis to make sure that the material is very thoroughly and completely mixed.

Water.—Determine the water by the Xylol Method as in the analysis of Greases (p. 358).

Total Ammonia.—Weigh out 30–40 grams of the paste in a beaker and transfer to a separatory funnel by means of hot 5% HNO_3. About 200 cc. of the acid should be employed. Shake out the paste thoroughly with the acid and let the layers separate. Draw off the solution into a liter volumetric flask. Repeat the shaking out of the melted paste in the funnel 3 times with fresh portions of about 200 cc. of the hot acid. Cool the solution in the flask to room temperature and dilute with water to the mark. Use aliquots of this solution for the determination of total NH_3, total Cl and Zn.

For the NH_3 determination, pipette 200 cc. into a Kjeldahl distilling flask, add a few drops of methyl orange and make distinctly alkaline with NaOH, adding at the same time a few grains of metallic Zn to prevent bumping. Distill in the usual manner, collecting the distillate in 50 cc. of 0.1 N acid. Titrate back the excess of acid with 0.1 N alkali and calculate the acid neutralized during the distillation to percentages of NH_3 and NH_4Cl.

CALCULATION.—1 cc. 0.1 N acid = 0.001703 gram NH_3.
= 0.005350 gram NH_4Cl.

Zinc Chloride.—Pipette 100 cc. of the acid solution into a 350-cc. beaker. Add a slight excess of NH_4OH and heat to boiling. Filter if there is a precipitate of Fe and Al hydroxides. Make the filtrate faintly acid with acetic acid; then add a large excess

of ammonium phosphate and boil the solution until the precipitate of $ZnNH_4PO_4$ is crystalline. Let settle until clear. Filter on a weighed Gooch crucible; wash with hot water and dry in the oven. Finally ignite strongly to constant weight and weigh as $Zn_2P_2O_7$. Calculate to percentage of $ZnCl_2$.

CALCULATION.—$Zn_2P_2O_7 \times 0.8943 = ZnCl_2$.

Total Chlorine.—It is not generally necessary to determine the total Cl unless it is desired to check up the previous determinations or unless NaCl is suspected to be present. For the determination, pipette 50 cc. of the HNO_3 solution into a clean porcelain dish or casserole. Add sufficient pure $CaCO_3$ to neutralize all the acid present and still have an excess of the $CaCO_3$ undissolved. Then add about 5 cc. of K_2CrO_4 indicator solution and titrate the Cl with 0.1 N $AgNO_3$ until a permanent reddish color appears in the solution. The end-point can best be determined in the presence of artificial light. Calculate the percentage of Cl.

CALCULATION.—1 cc. 0.1 N $AgNO_3 = 0.003546$ gram Cl.

NOTE.—The total Cl of course should check closely the amount of Cl equivalent to the $ZnCl_2$ and NH_4Cl determined. If it is in excess, the material should be tested for Na, and, if present, the excess Cl calculated to NaCl.

CALCULATIONS.—$NH_4Cl \times 0.6628 = Cl$.
$ZnCl_2 \times 0.5203 = Cl$.
$Cl \times 1.6486 = NaCl$.

FERTILIZERS

Directions for Sampling.—Each official sample sent to the laboratory shall consist of at least 1 pound of the material taken in the following manner: Employ a sampler that removes a core from the bag from top to bottom. Take cores from not less than 10 per cent of the bags present, unless this necessitates cores from more than 20 bags, in which case take a core from 1 bag for each additional ton represented. If there are less than 100 bags, sample not less than 10 bags. In lots of less than 10 bags, sample all bags. Thoroughly mix the portions taken on a clean oilcloth or paper, reduce by quartering to the quantity of sample required, and place in an air-tight container.

Mechanical Analysis of Bone and Tankage.—Transfer 100 grams of the original material to a sieve having circular openings

0.02 inch (0.5 mm.) in diameter and sift, breaking the lumps by means of a soft rubber pestle if the material has a tendency to cake. Weigh the coarse material remaining on the sieve and determine the fine portion by difference.

Preparation of Sample.—Pass the entire sample through a 10-mesh sieve previous to its subdivision for analysis. Reduce the gross sample by quartering to an amount sufficient for analysis. Transfer to a sieve having circular openings 0.04 inch (1 mm.) in diameter and sift, breaking the lumps with a pestle. Grind in a mortar the part remaining in the sieve until all the particles will pass through. Mix thoroughly and preserve in tightly stoppered bottles. Grind and sieve as rapidly as possible to avoid loss or gain of moisture.

Moisture.—Heat 2 grams, prepared as above, for 5 hours in a water oven at the temperature of boiling water. With potash salts, $NaNO_3$, and $(NH_4)_2SO_4$, heat at about 130° C. to constant weight. The loss in weight is considered as moisture.

Nitrogen.—Test for *nitrates* as follows: Mix 5 grams of the fertilizer with 25 cc. of hot water and filter. Cool and add to a portion of the solution 2 volumes of conc. H_2SO_4, free from HNO_3 and nitrous oxides. Let the mixture cool and add cautiously a few drops of a conc. solution of $FeSO_4$ down the side of the tube so that the fluids do not mix. If nitrates are present, the junction shows at first a purple, then a brown color; or if only a very minute quantity is present, a reddish color. To another portion of the solution add 1 cc. of a 1% solution of $NaNO_3$ and test as before to determine whether sufficient H_2SO_4 was added in the first test.

If nitrates are present, determine the various forms of nitrogen as described on page 87. If nitrates are absent, determine merely organic and ammoniacal nitrogen.

Phosphoric Acid (Gravimetric Method).—Reagents.—(*a*) *Ammonium Citrate Solution.*—Dissolve 370 grams of crystallized citric acid in 1500 cc. of water; nearly neutralize with conc. NH_4OH; cool, add NH_4OH until exactly neutral to corallin (a saturated alcoholic solution), and dilute sufficiently to make the sp. gr. 1.09 at 20° C. The volume will be about 2 liters.

(*b*) *Molybdate Solution.*—Dissolve 100 grams of molybdic acid in 144 cc. of conc. NH_4OH and 271 cc. of water; slowly and with

constant stirring pour the solution thus obtained into 489 cc. of conc. HNO_3 and 1148 cc. of water. Keep the mixture in a warm place for several days, or until a portion heated to 40° C. deposits no yellow precipitate of ammonium phosphomolybdate. Decant the solution from any sediment and preserve in glass-stoppered bottles.

(*c*) *Ammonium Nitrate Solution.*—Dissolve 200 grams of commercial NH_4NO_3, free from phosphate, in water and dilute to 1 liter.

(*d*) *Magnesia Mixture.*—Dissolve 22 grams of recently ignited calcined MgO in dil. HCl, avoiding an excess of acid. Add a little MgO in excess, and boil a few minutes to precipitate Fe, Al and P_2O_5; filter; add 280 grams of NH_4Cl, 261 cc. of conc. NH_4OH, and dilute to 2 liters. Instead of the solution of 22 grams of calcined MgO in HCl, 110 grams of crystallized $MgCl_2 \cdot 6H_2O$ may be used.

(*e*) *Dilute NH_4OH for Washing.*—Dilute 100 cc. of conc. NH_4OH to 1 liter.

(*f*) *Magnesium Nitrate Solution.*—Dissolve 320 grams of MgO in dil. HNO_3 (1 : 1), avoiding an excess of acid; then add a little MgO in excess; boil, filter from the excess of MgO, $Fe(OH)_3$, etc., and dilute with water to 2 liters.

Total Phosphoric Acid.—*Methods of Making Solution.*—Treat 2 grams of the sample by one of the methods given below. In the case of (*e*) 2.5 grams may be used. Cool the solution and dilute to 200 cc., or 250 cc. if a 2.5-gram sample is used. Mix and pour on a dry filter.

(*a*) Dissolve in 30 cc. of conc. HNO_3 and 3–5 cc. of conc. HCl and boil until organic matter is destroyed.

(*b*) Dissolve in 15–30 cc. of conc. HCl and 3–10 cc. of conc. HNO_3. This method is recommended for fertilizers containing much Fe or Al phosphate.

(*c*) Evaporate with 5 cc. of $Mg(NO_3)_2$ solution, ignite and dissolve in conc. HCl.

(*d*) Boil with 20–30 cc. of conc. H_2SO_4 in a Kjeldahl flask, adding 2–4 grams of $NaNO_3$ or KNO_3 at the beginning of the digestion and a small quantity after the solution has become nearly colorless, or adding the nitrate in small portions from time

to time. When the solution is colorless add 150 cc. of water and boil for a few minutes.

(*e*) Digest in a Kjeldahl flask with conc. H_2SO_4 and such other reagents as are used in either the plain or modified Kjeldahl or Gunning method for estimating nitrogen (see p. 87). Do not add $KMnO_4$, but after the solution has become colorless add about 100 cc. of water and boil for a few minutes.

(*f*) Ignite and dissolve in conc. HCl.

(*g*) Add 30 cc. of conc. HCl, heat, and add cautiously, and in small quantities at a time, about 0.5 gram of finely pulverized $KClO_3$ to destroy organic matter.

Determination.—Pipette an aliquot of the solution prepared above, corresponding to 0.25 gram, 0.50 gram or 1 gram into a 250-cc. beaker; add a slight excess of conc. NH_4OH and clear with a few drops of HNO_3, stirring vigorously. In case HCl or H_2SO_4 has been used as a solvent, add about 15 grams of dry NH_4NO_3 or a solution containing that amount. To the hot solution add 70 cc. of molybdate solution for every 0.1 gram of P_2O_5 that is present. Digest at about 65° C. for 1 hour and test the clear supernatant liquor for complete precipitation by the addition of more molybdate solution. Filter and wash with cold water or, preferably, with NH_4NO_3 solution. Dissolve the precipitate on the filter with dil. NH_4OH (1 :1) and hot water and wash into a beaker to a volume of not more than 100 cc. Nearly neutralize with conc. HCl, cool, and add magnesia mixture from a burette, slowly (about 1 drop per second), stirring vigorously. Add 15 cc. for each 0.1 gram of P_2O_5 present. After 15 minutes add 12 cc. of conc. NH_4OH. Let stand till clear (2 hours is usually enough), filter on a weighed Gooch crucible, wash with the weak NH_3 solution until practically free from chlorides; ignite first at a low heat and then intensely to whiteness or grayish white. Cool in a desiccator and weigh as $Mg_2P_2O_7$. Calculate to P_2O_5.

Calculation.—$Mg_2P_2O_7 \times 0.6379 = P_2O_5$.

Water-soluble Phosphoric Acid.—Place 2 grams of the sample on a 9-cm. filter, wash with successive small portions of water, allowing each portion to pass through before adding more, until the filtrate measures about 250 cc. If the filtrate is turbid, add 1–2 cc. of conc. HNO_3. Make up to any convenient definite

volume, mix well, use an aliquot* and proceed as under Total Phosphoric Acid above.

Citrate-insoluble Phosphoric Acid.—*Determination in Acidulated Samples.*—Heat 100 cc. of *strictly neutral ammonium citrate solution* (sp. gr. 1.09) to 65° C. in a 250-cc. flask placed in a warm water bath, keeping the flask loosely stoppered to prevent evaporation. The level of the water in the bath should be above that of the liquid in the flask. When the citrate solution in the flask has reached 65° C., drop into it the filter containing the washed residue from the water-soluble P_2O_5 determination, close tightly with a smooth rubber stopper and shake violently until the filter paper is reduced to a pulp, relieving the pressure by momentarily removing the stopper. Return the flask to the bath and maintain its contents at exactly 65° C. Shake the flask every 5 minutes. At the expiration of exactly 30 minutes from the time the filter and residue are introduced, remove the flask from the bath and immediately filter the contents as quickly as possible through a rapid filter paper. Wash with water at 65° C. until the volume of filtrate is about 350 cc., allowing time for thorough draining before adding new portions of water. Return the filter with contents to the digestion flask, add 30–35 cc. of conc. HNO_3, 5–10 cc. of conc. HCl and boil until all phosphate is dissolved. Dilute the solution to 200 cc., mix well, filter through a dry filter; take an aliquot of the filtrate and proceed as under Total Phosphoric Acid above.

Determination in Non-acidulated Samples.—In case a determination of citrate-insoluble P_2O_5 is required in non-acidulated samples, treat 2 grams of the phosphatic material, without previous washing with water, precisely in the way above described, except that, in case the substance contains much animal matter (bone, fish, etc.), the residue insoluble in ammonium citrate is to be dissolved by any one of the processes (*c*), (*d*) or (*e*) described under Total Phosphoric Acid.

Determination in Precipitated Phosphates.—Without previous washing with water, treat 1 gram of the material as directed above under Acidulated Samples.

* An aliquot corresponding to 0.5 gram of the original sample is generally a suitable amount.

Citrate-soluble Phosphoric Acid.—The sum of the water-soluble and citrate-insoluble, subtracted from the total, gives the citrate-soluble phosphoric acid (P_2O_5).

Phosphoric Acid (Optional Volumetric Method).—Reagents. (*a*) *Molybdate Solution.*—To 100 cc. of molybdate solution, prepared as directed above under Gravimetric Method, add 5 cc. of conc. HNO_3. Filter this solution immediately before using.

(*b*) *Standard NaOH or KOH Solution.*—Dilute 323.8 cc. of normal alkali, free from carbonates, to 1 liter. 100 cc. of the solution should neutralize 32.38 cc. of normal acid. 1 cc. is equal to 0.001 gram of P_2O_5 (1% of P_2O_5 on a basis of 0.1 gram of substance).

(*c*) *Standard Acid Solution.*—The strength of this solution is the same as, or one-half of, the standard alkali solution, and is determined by titrating against that solution, using phenolphthalein indicator. Either HCl or HNO_3 may be used.

(*d*) *Phenolphthalein Solution.*—Dissolve 1 gram of phenolphthalein in 100 cc. of alcohol.

Total Phosphoric Acid.—*Methods of Making Solution.*—Dissolve 2 grams according to methods (*a*), (*b*), (*c*) or (*g*), as described above under Gravimetric Method (preferably by (*a*), when these acids are a suitable solvent) and dilute to 200 cc. with water.

Determination.—(I) For percentages up to 5 use an aliquot corresponding to 0.4 gram of substance; for percentages between 5 and 20 use an aliquot corresponding to 0.2 gram; and for percentages above 20 use an aliquot corresponding to 0.1 gram. Add 5–10 cc. of conc. HNO_3, depending on the method of solution (or the equivalent in NH_4NO_3); add conc. NH_4OH until the precipitate that forms dissolves but slowly on vigorous stirring; dilute to 75–100 cc. and heat in a water bath to 45–50° C. For percentages below 5 add 20–25 cc. of freshly filtered molybdate solution; for percentages between 5 and 20 add 30–35 cc. of molybdate solution; and for higher percentages add sufficient to insure complete precipitation. Let stand in the bath, stirring occasionally, for 30 minutes, filter *at once* and wash twice with water by decantation, using 25–30 cc. each time, agitating the precipitate thoroughly and allowing to settle. Transfer to the filter and wash with cold water until the filtrate from 2 fillings

of the filter yields a pink color upon the addition of phenolphthalein and 1 drop of the standard alkali. Transfer the precipitate and filter to a beaker or flask, dissolve in a small excess of the standard alkali, add a few drops of phenolphthalein solution, and titrate with the standard acid.

(II) Proceed as in (I) to the point where the solution is ready to place in the water bath. Then cool the solution to room temperature, add molybdate solution at the rate of 75 cc. for each 0.1 gram of P_2O_5 present, place the stoppered flask containing the solution in a shaking or stirring apparatus and shake or stir for 30 minutes at room temperature. Filter at once, wash, and titrate as in the preceding method.

Water-soluble Phosphoric Acid.—Treat the sample according to directions given under the Gravimetric Method for Water-soluble P_2O_5. To an aliquot portion of the solution corresponding to 0.2 or 0.4 gram, add 10 cc. of conc. HNO_3, nearly neutralize with conc. NH_4OH, dilute to 60 cc. and proceed as under Determination (I) for Total P_2O_5, on page 768.

Citrate-insoluble Phosphoric Acid.—Make the solution according to the directions given under the Gravimetric Method for Citrate-insoluble P_2O_5 and determine the P_2O_5 in an aliquot corresponding to 0.4 gram as directed under the volumetric method for Total P_2O_5, Determination (I).

Citrate-soluble Phosphoric Acid.—The sum of the water-soluble and citrate-insoluble, subtracted from the total, gives the citrate-soluble P_2O_5.

Potash.—The K_2O is determined as on page 61.

Boric Acid.—See page 59.

Reference.—Association of Official Agricultural Chemists: "Methods of Analysis" (1925).

PHOSPHATE ROCK

General.—For purposes of mill control, in plants handling phosphate rocks from the mines, the only determinations ordinarily required are moisture, insoluble matter, iron oxide and alumina, and tricalcium phosphate. The latter is obtained by determining the total P_2O_5 and calculating it to $Ca_3(PO_4)_2$. This is known in the trade as B.P.L., or Bone Phosphate of Lime. Certain other determinations are sometimes required,

and in this method will be found procedures for Total Lime and Carbon Dioxide.

The majority of phosphate rocks contain $CaCO_3$; small amounts of $MgCO_3$; more or less $CaSO_4$, as well as CaF_2; combined water, and organic matter. Frequently also $CaCl_2$ is found, together with small amounts of the alkalies.

The Florida Pebble Phosphate generally contains 1.5–3.5% of combined water and organic matter; 5–10% of $CaCO_3$ and CaF_2; 2–5% of $Fe_2O_3+Al_2O_3$; 3–11% of insoluble matter (free silica and silicates); and 67–78% of $Ca_3(PO_4)_2$. Material containing 74% or more of B.P.L. goes into the "premium" class and commands an extra price.

Sampling.—As phosphate rock has a tendency to separate into fine and coarse portions on handling, it should always be sampled, when possible, by obtaining a cross-section of a falling stream. Samples taken from a loaded car are not representative. When it is necessary to sample a car, take the samples from at least 6 evenly distributed points within the car as far below the surface as possible, taking a gross sample of at least 25–50 pounds and preferably more. Crush the entire sample and quarter it down by means of a riffle, or similar quartering apparatus. Before making the final quartering, pulverize to about 8 or 10 mesh.

Preparation of Sample.—Make all determinations on a sample which has been ground to pass a 60-mesh sieve. Before weighing out the portions for analysis, mix the laboratory sample thoroughly by rolling and mixing on oilcloth or paper.

Free Moisture.—Dry a 5-gram sample for 2 hours at 105° C. Cool in a desiccator, weigh, and consider the loss as free moisture.

Insoluble Silicious Matter.—Boil 2.5 grams in a 250-cc. beaker with 25 cc. of dil. aqua regia until no more brown fumes are evolved. Filter off the insoluble matter, collecting the filtrate in a 250-cc. volumetric flask, and wash thoroughly. Ignite and weigh the residue. Ordinarily it is not necessary to differentiate between free and combined silica.

Dilute Aqua Regia.—Pour 500 cc. of conc. HCl and 500 cc. of conc. HNO_3 into 1000 cc. of water.

Iron Oxide and Alumina.—Dilute the above filtrate to 250 cc. in the volumetric flask, mix well, and pipette out 50 cc. (equivalent to 0.5 gram of the original sample). Make alkaline with

NH_4OH, add a few drops of methyl orange indicator, dilute to double the volume and make *just* acid with dil. HCl (1:1). It is necessary to add sufficient acid to dissolve all the precipitate. Heat nearly to boiling and add 20 cc. of ammonium acetate solution, made by adding 5 cc. of glacial $HC_2H_3O_2$ to 15 cc. of a neutral saturated $NH_4C_2H_3O_2$ solution. Filter off the precipitate and wash thoroughly with hot water. Dissolve this precipitate through the filter with hot dil. HCl (1:3) into another 250-cc. beaker and wash thoroughly. Add 10 cc. of 10% $(NH_4)_2HPO_4$ solution, heat to boiling and precipitate with NH_4OH. Filter and wash with 2% NH_4NO_3 solution. Dry the paper and contents in the oven. Transfer as much as possible of the precipitate to a glazed paper. Ignite the filter paper in a weighed platinum crucible. Then add the bulk of the precipitate, ignite, cool in a desiccator and weigh as $FePO_4+AlPO_4$.

Fuse the residue with $KHSO_4$. Dissolve in water and add sufficient H_2SO_4 to make a 5% solution. Pass through the Jones reductor and titrate with 0.1 N or 0.05 N $KMnO_4$. Calculate the Fe_2O_3 thus found to $FePO_4$. Subtract this from the original weight of the precipitate and calculate the remaining $AlPO_4$ to Al_2O_3.*

CALCULATIONS.—1 cc. 0.1 N $KMnO_4$ = 0.007984 gram Fe_2O_3.

$Fe_2O_3 \times 1.89 = FePO_4$.

$AlPO_4 \times 0.4177 = Al_2O_3$.

Tricalcium Phosphate.—There are 3 usual methods of making this determination: (1) the gravimetric method, which depends upon dissolving the yellow phosphomolybdate precipitate and reprecipitating the phosphorus in the form of $MgNH_4PO_4$, which is ignited and eventually weighed as $Mg_2P_2O_7$; (2) the volumetric method, titrating the yellow precipitate with alkali; and (3) direct weighing of the yellow precipitate. The first 2 methods are considered the most reliable. Where a number of determinations is made daily and where speed is also necessary, the volumetric method is preferable. Where only occasional determinations are required, however, it is hardly worth while to make up and standardize the solutions required for this method and in such cases the gravimetric method should be used.

* The presence of fluorides tends to cause low results for Al_2O_3 by this method, but for most purposes the results are sufficiently accurate.

(1) Gravimetric Method.—*Solutions.*—Ammonium Molybdate.—Dissolve 100 grams of molybdic acid in dil. NH_4OH (144 cc. of conc. NH_4OH and 271 cc. of water); pour this solution slowly and with constant stirring into a mixture of 489 cc. of conc. HNO_3 and 1148 cc. of water. Keep in a warm place for several days or until a portion heated to 40° C. deposits no yellow precipitate of ammonium phosphomolybdate. Decant the solution from any sediment and preserve in glass-stoppered bottles. (This is the same solution as used in fertilizer analysis, p. 764.)

Corallin Indicator.—Make a saturated solution in equal parts of 95% grain alcohol and water. (Specially denatured alcohol formula 30 may be used.)

Magnesia Mixture.—Dissolve 110 grams of $MgCl_2 \cdot 6H_2O$ and 280 grams of NH_4Cl in water. Add 261 cc. of conc. NH_4OH, make up to 2000 cc. and filter. Let a new solution stand at least 10 hours before filtering.

Determination.—Evaporate 2.5 grams of the sample to a thick syrup on the hot plate with an excess of conc. HCl. Add about 10 cc. of HCl and again evaporate to syrup. Avoid baking. Take up with 50 cc. of dil. HNO_3 (1 : 1) and boil for about 5 minutes. Dilute to 100 cc. in a volumetric flask. Pipette 50 cc. into a 400-cc. beaker, dilute to about 100 cc. and add 30 cc. of conc. NH_4OH and then 40 cc. of conc. HNO_3. (15 grams of NH_4NO_3 may be added to the solution in place of the NH_4OH and HNO_3.) Heat the clear solution, slightly acid with HNO_3, to 65° C. and add 180 cc. of ammonium molybdate solution. Add the latter very slowly with continuous stirring, as otherwise an extremely fine precipitate will form which is difficult to filter. Let stand at a temperature of 65° C. for 0.5 hour, then filter, and wash three times by decantation with 1% HNO_3. In order to make certain that the washing is complete, about 200 cc. of water should be used subsequent to the washing with HNO_3.

Dissolve the precipitate through the filter into a 250-cc. beaker with the least possible amount of dil. NH_4OH and wash thoroughly, keeping the volume within 100 cc. Add 1 or 2 drops of corallin indicator and then dil. HCl until the purple color is just destroyed. Cool and add 20 cc. of magnesia mixture, at the rate of 1 or 2 drops per second, with constant stirring. Let stand 15

minutes; then add 25 cc. of dil. NH_4OH. Let stand 2 hours, stirring occasionally. Filter on a Gooch crucible, wash with 3% ammonia water, then with a few drops of NH_4NO_3 solution, dry in the oven and then ignite to constant weight as $Mg_2P_2O_7$. Calculate to P_2O_5 and to $Ca_3(PO_4)_2$.

CALCULATIONS.—$Mg_2P_2O_7 \times 0.6379 = P_2O_5$.
$Mg_2P_2O_7 \times 1.3932 = Ca_3(PO_4)_2$.

(2) VOLUMETRIC METHOD.—*Solutions.*—Molybdate Solution.—Use the same solution as for the Gravimetric Method, adding to it 5 cc. of conc. HNO_3 for each 100 cc. of the solution immediately before use.

Ammonium Nitrate.—Dilute 1200 cc. of conc. NH_4OH with 1 liter of water. Dilute 1340 cc. of conc. HNO_3 with 1 liter of water. Pour the NH_4OH solution into the diluted HNO_3 slowly and with constant stirring. Make the mixture in an earthen crock or large Pyrex glass flask as considerable heat is generated.

Standard Caustic (0.3238 N).—Dissolve 200 grams of stick KOH (or 145 grams of stick NaOH) in 400 cc. of water. Add an excess of $Ba(OH)_2$ solution and let stand 2 hours or more. Filter, add to the filtrate an excess of saturated K_2SO_4 or Na_2SO_4 solution, and again filter. The filtrate will be a solution of KOH free from carbonate and containing harmless K_2SO_4. Measure accurately 10 cc. into a 100-cc. volumetric flask and dilute to the mark with distilled water, free from CO_2. Titrate 10 cc. with the standard HNO_3. The KOH should be just twice the strength of the HNO_3. Suppose it requires 9.40 cc. of HNO_3. Then 9.40 should equal 4.70 cc. of the caustic solution. The ratio for 2 liters would then be $1.0 : 4.70 = x : 2000$, and $x = 425.5$. Then dilute 426 cc. of the strong caustic to 2000 cc. with distilled water free from CO_2. This solution will contain 36.34 grams of KOH (or 25.91 grams of NaOH) in 2 liters.

Standard HNO_3 (0.1619 N).—Dilute 100 cc. of conc. HNO_3 to 1000 cc. Then dilute 203.3 cc. of this solution to 2000 cc. Titrate the latter against the caustic solution.

Standardization of Solutions.—First standardize the caustic against the HNO_3 by titrating 25 cc. of the former against the latter with phenolphthalein; then standardize the caustic against a standard sample containing a known amount of

$Ca_3(PO_4)_2$ in exactly the same manner as described below under Determination.

If made up to the proper strength, 1 cc. of the caustic will require exactly 2 cc. of the standard acid and 1 cc. of the latter will be equivalent to about 1% of $Ca_3(PO_4)_2$ when using a 0.1-gram sample. Where a large number of determinations is made daily, considerable time may be saved in calculations by adjusting the solutions in this way.

NOTE.—Since the results obtained by the volumetric method are influenced by numerous factors such as the composition of the molybdate solution, the temperature of precipitation, the extent to which the solution is stirred after precipitating, and the length of time between precipitation and filtration, it is necessary, in order to obtain accurate results, to standardize the solutions frequently against a phosphate rock, the $Ca_3(PO_4)_2$ content of which has been accurately determined by the gravimetric method previously described. The phosphate content of this standard rock must be reasonably close to that of the sample under analysis and it should be used as a control or blank determination every time an unknown sample is analyzed, or with each set of samples run at the same time. If the result obtained on the standard sample varies from its known phosphate content, the results obtained on the unknown samples should be corrected accordingly.

Determination.—Pipette into a 250-cc. beaker 10 cc. of the filtrate from the Insoluble Matter determination (equivalent to 0.1 gram). Add 65 cc. of NH_4NO_3 solution and precipitate by the addition of 45 cc. of molybdate solution. Make the precipitation at room temperature unless the temperature is below 30° C., in which case warm the solution to 30–35° C. before precipitating. Stir for 15 minutes, preferably with a mechanical stirrer; then filter, either on filter paper or by suction through a carbon filtering tube provided with a circular porcelain disk and asbestos mat. It is convenient, where the latter arrangement is used, to attach a wire to the disk and run it down through the stem of the filtering tube. This makes it possible, after filtration and washing is completed, to push the disk together with the precipitate out of the mouth of the tube into the beaker for titration.

Transfer the precipitate to the filter paper or filtering tube and wash the beaker containing the precipitate free from acid. Then wash the precipitate itself not less than ten or twelve times in order to make certain that it is *acid free.* Transfer the washed precipitate to the original beaker, add 20–25 cc. of water and then

run in standard caustic solution, 5 cc. at a time, until the yellow precipitate is completely dissolved. Finally titrate the excess alkali with standard HNO_3, using phenolphthalein indicator. From the amount of alkali consumed calculate the percentage of $Ca_3(PO_4)_2$.

Total Lime.—Evaporate 1 gram of the sample twice with HCl and take up with HNO_3 as previously described in the gravimetric method for Tricalcium Phosphate. Dilute to 100 cc. in a volumetric flask. Transfer 25 cc. to a small beaker and add 10 cc. of dil. H_2SO_4 (1 : 1). Add 100 cc. of alcohol (No. 30 special denatured) and let stand for at least 1 hour. Filter, wash with alcohol, dry, ignite, and weigh as $CaSO_4$. Calculate to CaO.

CALCULATION.—$CaSO_4 \times 0.4119 = CaO$.

Carbon Dioxide.—The apparatus for this determination is shown in Fig. 40. Before starting the analysis, run a blank on

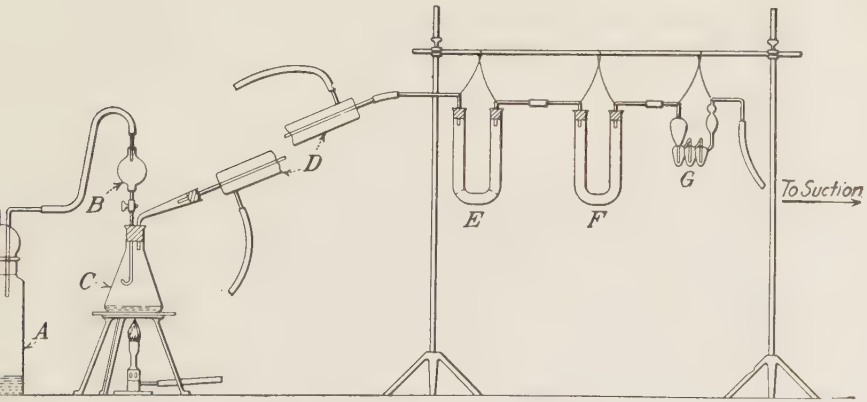


FIG. 40.—Apparatus for Determination of CO_2 in Phosphate Rock. (A = gas washing bottle with 40% KOH solution; B = 100 cc. separatory funnel; C = 300 cc. Erlenmeyer flask; D = 12–15″ Liebig condenser; E = plain 6″ U-tube filled in center with anhydrous $CuSO_4$, on each side with anhydrous $CaCl_2$; F = plain 6″ U-tube filled with anhydrous $CaCl_2$; G = Geissler KOH bulb with 40% KOH solution.

the apparatus to see that the weight of the KOH absorption bulb is constant. Do this by drawing air through the apparatus for 10 minutes, then weighing the KOH bulb. Continue the air for 0.5 hour longer and weigh again. Repeat until the weight remains constant.

When the weight of the bulb is constant within ± 0.0005 gram, weigh out 5 grams of the sample into the 300-cc. Erlenmeyer flask and cover with water. Close the stop-cock in the separatory funnel and place in it 50 cc. of dil. HCl (1 : 1). Connect the apparatus, start a current of air at the rate of about 3 bubbles per second, open the stop-cock and run in the acid slowly. As soon as the acid is all in the flask, supported on an asbestos gauze mat, place a burner under it. Regulate the burner so that the flame is not more than 1 inch long and without blast; in other words, use just sufficient heat to boil the solution gently, otherwise the back pressure will cause trouble. By watching the inlet tube of the KOH purifying bottle, one can tell when there is too much back pressure and either decrease the heat or increase the rate of flow of air.

After the solution comes to ebullition, boil for about 2 minutes, which should effect complete decomposition of all carbonates. Then remove the heat and pass air through the apparatus for about 15 minutes to sweep out all CO_2. Weigh the KOH bulb and calculate the increase in weight to percentage of CO_2.

BAUXITE

General.—The essential ingredient of bauxite is Al_2O_3 and it is widely used in making aluminum sulfate. It also contains varying amounts of iron oxide and silicious matter and generally an amount of TiO_2 varying from a trace to several per cent. A high-grade bauxite should contain at least 52% of Al_2O_3 on the dry basis.

Before analysis, the sample should be thoroughly mixed and ground to a fine powder.

Water and Organic Matter.—Ignite 0.5 gram in a weighed platinum crucible, first over a Bunsen burner and finally with a blast lamp to constant weight. Calculate the percentage loss in weight.

Silica.—Weigh 1 gram of the powdered material into a 250-cc. beaker and add 50 cc. of dil. H_2SO_4 (1 : 1). Digest on the hot plate with the beaker covered for 3 hours and then evaporate until white fumes come off strongly. Cool *thoroughly*, add 100 cc. of water, boil for 10 minutes and then filter and wash with hot water, saving the filtrate. Ignite the insoluble residue in a

platinum crucible (which need not be weighed) and finally blast for 15 minutes. Cool in a desiccator and weigh. This residue consists mainly of SiO_2 with a little TiO_2, Fe_2O_3 and Al_2O_3.

To determine the SiO_2, treat the insoluble matter in the platinum crucible with about 1 cc. of dil. H_2SO_4 and then fill the crucible half full of HF. Evaporate off the latter and repeat the operation once. Ignite the residue gently to drive off all H_2SO_4. Then heat in the full flame of a Meker burner, cool in a desiccator and weigh. Report the loss in weight by the HF treatment as SiO_2.

Fuse the residue in the crucible with about 1 gram of $KHSO_4$. Cool, and place the crucible with the fused mass in the beaker containing the H_2SO_4 filtrate from the original treatment for SiO_2. Heat the solution nearly to boiling. There will probably be a slight residue of SiO_2 left. If so, filter it out, ignite, cool, weigh, and add to the SiO_2 previously obtained.

Iron, Aluminum, and Titanium Oxides.—Dilute the above filtrate to 250 cc. in a volumetric flask and, after thoroughly mixing, pipette out 50 cc. into a 400-cc. beaker. Add 250 cc. of water and 10 cc. of conc. HCl. Then add a few drops of methyl red indicator (0.2% alcoholic solution) and heat just to boiling. Carefully add conc. NH_4OH until nearly neutralized, then add dil. NH_4OH until the color of the solution changes to a distinct yellow. Boil for 1 or 2 minutes and filter at once. Wash the precipitate thoroughly with hot 2% NH_4Cl solution, and finally once with hot water. Dry the precipitate, ignite over the blast in a weighed platinum crucible, cool and weigh as $Al_2O_3+Fe_2O_3+TiO_2$. Correct for aliquoting and calculate to percentage.

Titanium Oxide.—Determine the titanium by one of the following methods. The colorimetric method is preferable for small amounts.

(*a*) Gravimetric Method.—Pipette 100 cc. of the H_2SO_4 solution (equivalent to 0.4 gram) into a 500-cc. beaker and add NH_4OH till a slight permanent precipitate forms. Redissolve this with a few drops of H_2SO_4 and dilute the solution to about 400 cc. Boil thoroughly. (If the solution contains much iron it will be of a yellow color.) Add 10 cc. of a saturated NH_4HSO_3 solution (made by passing a current of SO_2 into conc. NH_4OH) and continue the boiling for at least 1 hour, keeping the volume

as near constant as possible. This will precipitate the titanium as TiO_2. If considerable TiO_2 is present it may be necessary to continue the boiling for several hours to obtain complete precipitation. Filter out the TiO_2 precipitate, using a filter similar to C. S. & S. blue ribbon, and wash with hot water containing a little acetic acid. Dry, ignite in a weighed platinum crucible, cool in a desiccator, and weigh as TiO_2.

NOTE.—If the precipitate is yellow, it indicates the presence of Fe_2O_3. In this case fuse with about 1 gram of $KHSO_4$, take up the fusion with water containing 5% of H_2SO_4, determine the iron as described below under Ferric Oxide and correct accordingly.

(*b*) COLORIMETRIC METHOD.—Pipette 50 cc. of the H_2SO_4 solution (equivalent to 0.2 gram of the sample) into a beaker. Precipitate the Ti, Al, and Fe together with NH_4OH, as previously described. Wash the precipitate moderately and dissolve in 5% H_2SO_4; then oxidize in the cold with about 5 cc. of H_2O_2 (ordinary 3% solution). Dilute to 100 cc. in a volumetric flask with 5% H_2SO_4, and match the color with a standard Ti solution (similarly peroxidized) in 100-cc. Nessler tubes, making proper corrections for dilution.

NOTE.—The color due to the Fe salts must be corrected for. The simplest method of doing this, although it is not strictly accurate in the presence of considerable amounts of Fe, is to consider 0.1 gram of Fe_2O_3 in 100 cc. of 5% H_2SO_4 solution equivalent to 0.0002 gram of TiO_2 in 100 cc., when oxidized by H_2O_2. The correction to be applied may be figured from the amount of Fe_2O_3 as determined separately.

Standard Titanium Solution.—Potassium titanium fluoride, K_2TiF_6, serves as the best starting-point for the preparation of the standard solution. Place in a platinum dish sufficient of the salt to make 500–1000 cc. of a standard sulfate solution containing 1 gram of TiO_2 per liter and evaporate several times with conc. H_2SO_4, without bringing to dryness, until the fluorine is completely expelled. Take up the residue with water containing enough H_2SO_4 to make at least 5% when fully diluted. Then determine the TiO_2 gravimetrically in 2 portions of 50–100 cc. of the prepared solution by diluting further, heating to boiling and precipitating with NH_4OH. Filter, wash thoroughly with hot water, ignite, blast, cool, and weigh as TiO_2. Duplicates should agree very closely. From the average of the weight found calculate the

strength of the solution in milligrams of TiO_2 per cc. The solution should be preserved in a bottle, the stopper of which is coated with vaseline, and the needed quantities should always be withdrawn with a pipette, never poured. In making an analysis, mix 5 cc. of the standard solution (or 10 cc. if desired) with a sufficient quantity of H_2O_2 and dilute with 5% H_2SO_4 to 50 or 100 cc. in a volumetric flask, according to the original volume taken. Each cc. of the diluted standard will then contain approximately 0.1 milligram of TiO_2 (the exact amount being determined by the analysis).

Ferric Oxide.—Pipette 50 cc. or 100 cc. of the original sulfate solution into a beaker and run through a Jones reductor, collecting the reduced solution in a suction flask containing a solution of ferric alum. The tip of the reductor must dip below the surface of the ferric alum solution. Have the solution hot and precede it in the reductor by hot 5% H_2SO_4 solution. Titrate the Fe and Ti together with 0.01 N $KMnO_4$. Deduct the permanganate equivalent to the TiO_2 and also the amount required for a blank run under similar conditions (substituting 50 cc. of 10% H_2SO_4 for the titanium-iron solution) and calculate the difference to Fe_2O_3.

CALCULATIONS.—0.001 gram TiO_2 = 1.25 cc. 0.01 N $KMnO_4$.
1 cc. 0.01 N $KMnO_4$ = 0.0008 gram Fe_2O_3.

Alumina.—Calculate alumina by difference, subtracting from the combined oxides the sum of the Fe_2O_3 and TiO_2, as determined above.

NOTES. —(1) Vanadium and Cr interfere with the titration of Fe and also of Ti. Vanadium, however, does not ordinarily occur in bauxite and its presence would be indicated by an "off" color (brownish or reddish) of the peroxidized solution.

(2) Any P_2O_5 will be included in the precipitate of the combined oxides and a separate correction would have to be made for it. It is very unusual, however, to find more than traces in bauxite.

NATIONAL METHOD

The so-called "National Method" of analyzing Bauxite is in quite common use in this country. It is a convenient method when a complete analysis is not desired. The procedure is as follows:

Grind the sample until it will pass a 100-mesh sieve and dry at 105° C. Weigh out 2 grams of the dry material and place in a Kjeldahl digestion flask together with 20 grams of dil. H_2SO_4 (3 : 2), connect to a reflux condenser and boil for 3 hours. Cool immediately, dilute with water, filter and wash into a 500-cc. volumetric flask. Dilute to the mark with water at room temperature and mix well.

Alumina.—To 50 cc. of the above solution, add 10 cc. of dil. HCl, make slightly alkaline with NH_4OH, and let stand on the steam bath for 10 minutes. Filter through a 15-cm. paper, using a filter pump and slight suction; wash four times with hot water and finally suck the precipitate dry. Ignite at low heat in a weighed platinum crucible and, when the paper is consumed, carefully grind down any lumps in the crucible with a smooth glass rod. Then ignite to constant weight in a blast lamp and cool in a desiccator before weighing. Subtract from the weight obtained the amount of Fe_2O_3 as determined below, and report the difference as Al_2O_3.

Iron Oxide.—To 100 cc. of the acid solution add a little $KClO_3$, evaporate to dryness, dissolve (adding a small amount of moderately strong HCl if necessary), and destroy organic matter by heating with an excess of $KMnO_4$. Neutralize with NH_4OH, reduce the iron with a current of SO_2, boil off the excess of SO_2 and add a little $HgCl_2$ solution to insure removal of the last traces. Cool, acidify with H_2SO_4, and titrate with standard $KMnO_4$ solution.

References.—The above method is based on the method of the Aluminum Company of America, somewhat modified by experience in this laboratory. See also *U. S. Geol. Survey, Bull.* 700, 107–109, 155–162.

CARBOLINEUM AND SIMILAR WOOD-PRESERVING OILS

General.—About 1 quart of oil is required for a complete analysis. It is possible to make a single analysis on about a pint, but the above amount provides for a check determination in case anything happens to the first. Before analyzing, thoroughly liquefy the sample and mix it well by shaking and stirring.

Specific Gravity at 38° C.—Fill a hydrometer cylinder with the liquefied oil and place the cylinder in water, then heat until the temperature of the oil is several degrees higher than 38° C.

Let the water cool until the oil has reached a temperature of 38° C. Thoroughly stir the oil, place a hydrometer in the cylinder, and carefully observe the reading. Take care that the hydrometer does not touch the bottom or sides of the cylinder when the reading is made.

Condition at 38° C.—Heat about 100 cc. of the oil in a beaker to a temperature of not less than 45° C. and let the oil cool gradually. When a temperature of 38° C. is reached, examine the oil carefully by means of a glass stirring rod. No solid crystalline particles should appear on the rod when withdrawn from the oil. A cloudiness of the oil may be disregarded.

Flash Point.—Place an evaporating dish, about 4 or 4.5 inches in diameter, on an asbestos diaphragm of sufficient size to extend several inches beyond the dish. Cut a hole in the center of the diaphragm about half the maximum diameter of the dish and set the dish in it. Cover the bottom of the dish with dry sand to a depth of about 0.25 inch and place an evaporating dish, about 3 inches in diameter, on the sand. Fill the remaining space between the two dishes with sand until it reaches nearly to the rim of the inner dish. Arrange a thermometer so that the bulb is inside and about 0.25 inch above the bottom of the inner dish. Pour some of the liquefied oil into the dish until it is about $\frac{3}{4}$ full. Place a low flame beneath the sand bath, with a suitable guard to protect it from draughts, which should be carefully excluded from the vicinity of the testing apparatus. Heat so that the temperature of the oil will increase about 3° C. per minute. Apply a small flame just above the surface of the oil for every 2° rise of temperature until the flame flashes across the surface of the oil. The temperature of the oil when this occurs is the flash point. Report results in Centigrade degrees.

Burning Point.—Continue the heating and the application of the testing flame until the oil ignites and burns for 5 seconds or more. The temperature at which this occurs is the burning point.

Water.—Weigh out 10 grams of the original oil into a 300-cc. Erlenmeyer flask. Add to this 75 cc. of Xylol which has previously been saturated with water and proceed as directed on page 358.

Fractionation.—Arrange the apparatus for distillation as shown in Fig. 41.

For the distillation a use 200-cc. Pyrex glass, round-bottomed, fractionating flask which shall satisfy the following requirements:

It shall hold not less than 190 cc. nor more than 210 cc. when filled to the base line of the neck. The bulb shall be $2\frac{7}{8}$ inches in diameter. The neck shall be $\frac{13}{16}$ inch in diameter and 4 inches in length. The side-arm shall be taken off at a point equidistant from the top and base of the neck.

Connect an air condenser 14 inches long and 0.5 inch in diameter to the side-arm of the flask, as shown in the figure, in order to insure complete condensation of the distillate.

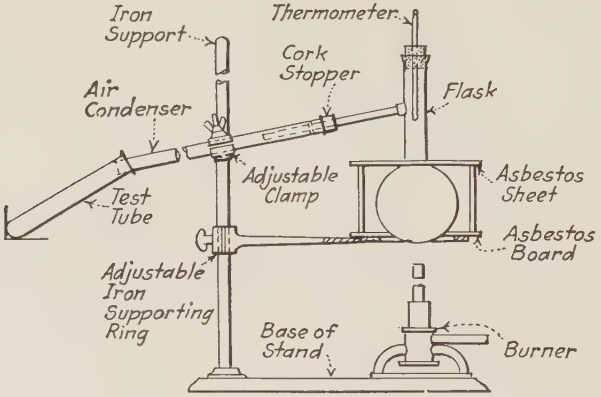


FIG. 41.—Distillation Apparatus for Carbolineum.

Before setting up the apparatus, weigh the flask accurately and then pour into it, by means of a stirring rod, exactly 100 grams of the thoroughly liquefied and mixed oil.

Before beginning the distillation, fit the thermometer through the stopper in the neck of the flask so that the top of the bulb comes just below the lower edge of the side-arm tube. Do not move the thermometer during the distillation. Rest the flask in a hole $1\frac{3}{4}$ inches in diameter in an asbestos board supported on the ring stand. To protect the flask from draughts, provide an asbestos shield surrounding the flask, resting on the asbestos board, and rising to the level of the top of the bulb. Play an open flame on the bottom of the flask and apply the heat so regulated that the distillate passes over at the rate of about 1 drop per second.

It is to be understood that the distillation has commenced as soon as the first drop of the distillate appears in the delivery tube of the flask and ended when a temperature of 360° C. is reached.

NOTE.—The distillation of some samples of oil may be accompanied, especially during the first few moments, by a violent spattering of the liquid, and small quantities may go over into the test-tubes. This can usually be avoided by inserting a small piece of unglazed porcelain in the flask before commencing the distillation.

Distillate.—Weigh up accurately 7 test-tubes properly labeled for identification. Collect the fractions of the distillate in these test-tubes according to the temperatures given in Table XXXV.

TABLE XXXV—DISTILLATION FRACTIONS FOR CARBOLINEUM

Test-tube No.	Temperature, °C.	Fraction
1	Up to 205	Water, tar acids, naphthalene (if present)
2	205–235	Tar acids, naphthalene
3	235–270	
4	270–300	
5	300–315	Anthracene, anthracene oil
6	315–330	
7	330–360	
	Residue above 360	Residue in flask

After completion of the distillation, drive over all the material which is in the air condenser by playing a flame over the condenser. Weigh up each of the test-tubes and also weigh the flask with the residue after it is cool.

Calculate the percentages of the different fractions and add them together. The sum should be within 0.5% of 100%, except when there is a considerable amount of water present. If the loss, after carefully checking the figures, is found to be large when a sample containing little water or other low-boiling constituents is distilled, repeat the distillation.

Sulfonation Residue.—Carry out this test on the fractions of Carbolineum distilling between 300 and 330° C. (For Dead Oil of Coal Tar the test should be carried out on the fractions distilling between 300 and 360° C.) Transfer the fractions to a

large-mouthed round flask of about 250-cc. capacity. Then add 4–5 volumes of conc. H_2SO_4 for each volume of distillate under test. Heat for about 5 minutes with frequent shaking; then let stand about $\frac{1}{2}$ hour, shaking at intervals. Slowly pour the mixture of acid and oil into a liter beaker containing enough water to dissolve the sulfonic acids formed. When cool, transfer from the beaker to a separatory funnel and let settle for 1 hour, or longer if necessary, until the undissolved oil separates clearly. Draw off and reject the water containing the sulfonic acids. Transfer all the oily residue to a tube graduated to 0.1 cc. and measure its volume (see note).

If there should be a heavy insoluble residue, it is probable that the sulfonation has been incomplete. In this case, add common salt to the water until the residue rises to the top of the water solution. Separate the unsulfonated oil and submit it again to the sulfonating treatment. In case the residue exceeds the maximum allowed by the specifications, treat it with a 10% NaOH solution. If the residue is soluble in this reagent, the sulfonation test may be regarded as giving negative results. Separate and measure the residue of oil remaining after the treatment with NaOH solution. The amount of residue thus found is reported as Sulfonation Residue. It is a measure of any mineral oil present.

Note.—As the sulfonation residue is generally very small, we have found it convenient to draw off all but about 10 cc. of the lower acid layer from the separatory funnel and then drain the liquid remaining in the funnel into a "color carbon tube" graduated 0–25 cc. in 0.1 cc. Rinse the funnel out with ether and drain this into the tube. Then immerse the tube in warm water to a level slightly above the level in the tube. Blow a gentle current of air into the tube by means of a smaller glass tube reaching nearly to the surface of the inner liquid. Slowly raise the temperature of the outside water by pouring in hot water (keep flames away) until the ether boils. When all ether has been evaporated off, cool to room temperature and read the volume of the upper layer.

Tar Acids.—Carry out this determination on the fractions distilling below 300° C. Transfer them to a beaker of about 300-cc. capacity and thoroughly mix by stirring. Add 30 cc. of NaOH solution (17–18%) to the oil and heat the whole gently for 2 minutes, with frequent stirring. Transfer the mixture to a large separatory funnel and shake vigorously for at least 1 minute

Then let the mixture settle and draw off and save the NaOH solution which forms the lower liquid layer.

Repeat this operation a second and third time, using 20 cc. of NaOH solution each time. Mix the 3 NaOH solutions together, boil vigorously for 5 minutes and let cool. Transfer to a special separatory funnel with a tube graduated to 0.1 cc. Add dil. H_2SO_4 (1 : 3) until the solution is acid to litmus paper. About 35 cc. of acid will be required and care must be taken that the solution be kept cool while adding the acid. Let stand until the tar acids are well separated and read their volume (upper layer). Compute the percentage by dividing this volume by the *volume* of the oil taken for distillation; *viz.*, the original *weight* of oil divided by its sp. gr.

Insoluble in Benzene.—Weigh out a 10-gram portion of the original oil into a small beaker (about 100–150-cc. capacity), add 20 cc. of benzene (commercial benzol) and filter through a weighed alundum (or Gooch) crucible with suction. Wash the residue in the crucible with benzene until the washings run colorless; dry the crucible at 110° C., weigh and compute the percentage of insoluble material.

Ash.—Weigh carefully into a weighed porcelain crucible about 2 grams of the oil, and heat cautiously over a low flame until the oil ignites. When the flame from the burning oil ceases, increase the heat, and after all organic matter has apparently burned off, cool and weigh. Reheat and reweigh, until a constant weight is obtained.

Acetic Acid and Acetates (Qualitative Test.)—Place about 5 cc. of the oil in a test-tube and add about $\frac{1}{2}$ of its volume of alcohol. Then add conc. H_2SO_4 slowly, drop by drop, with frequent shaking until the liquid is hot to the touch. If acetic acid or acetate is present, the characteristic odor of ethyl acetate will develop.

To make certain of this odor always run a blank at the same time, adding to another portion of 5 cc. of the original oil in the test-tube a drop of acetic acid, and then carry through the test as above described.

NOTES. (1) The apparatus should be thoroughly cleaned after each distillation. To remove the residue from the flask, add some of the oil and heat until the residue is all dissolved. Then pour out the oil and wash the flask with hot water and Sapolio.

(2) The above method, with the exception of the determination of water, is obtained from Specification L-3432 of the Western Electric Company: "Analysis of Carbolineum and Similar Wood Preserving Oils," Nov. 10, 1911.

GYPSY MOTH CREOSOTE

Specific Gravity.—Determine the sp. gr. at 15.5° C. with a Westphal balance.

Fractional Distillation.—Distill 200 cc. of the creosote in a 250-cc. side-neck distilling flask having a thermometer inserted through the cork stopper in the neck with the bulb opposite the side tube of the flask. Conduct the distillation at the rate of approximately 2 drops per second, collecting each fraction in a small weighed flask. Take the following fractions and report the percentages by weight:

150–200° C.
200–245° C.
245–270° C.
270–320° C.
Residue above 320° C.

Examine the residue above 320° C. and note whether heavy oils have been added to the creosote.

Tar Acids.—Employ the distillate obtained above, by distilling up to a temperature of 320° C., and determine the tar acids as described on page 784. Report the percentage of tar acids by volume.

COAL-TAR ROOFING PITCH

General.—The methods for testing materials like coal-tar pitch must necessarily be more or less empirical. The following procedures are from specifications prepared for the Supervising Architect of the U. S. Treasury Department and are valuable in comparing different samples where straight run coal-tar pitch is desired.

Melting Point.—Determine the melting point by the Cube Method, as described on page 792.

Insoluble in Benzene.—Digest 10 grams of the pitch in pure toluene on the steam bath, and decant through a filter cup consisting of 2 No. 575 C. S. & S. hardened filter papers (previously

dried at 105° C. in a weighing bottle and weighed). Transfer the residue to this filter, and extract with pure benzene in any form of extraction apparatus which insures hot extraction, until the washings run through practically colorless. Dry and weigh the papers plus the residue, and calculate the percentage of insoluble matter.

Specific Gravity.—Make a small ball of the material weighing several grams. Make sure that no air bubbles are occluded within it. Determine the sp. gr. of this by weighing in air and then submerged in water at 60° F., as described under the Displacement Method (p. 789).

Loss on Evaporation.—Determine the loss in weight of 100 grams of pitch placed in a flat nickel dish 2 inches in diameter, and subjected to a temperature of 325° F., for 7 hours.

Specific Gravity of Distillate to 670° F.—Distill from a side-neck flask an unweighed quantity of the sample (50–100 grams). Have the bulb of the thermometer opposite the side-neck of the flask and continue the distillation until the temperature reaches 670° F. Determine the sp. gr. of the distillate with a pycnometer at 140° F., compared with water at the same temperature.

NOTES.—(1) This method is obtained from the *Amer. Ry. Eng. Assoc., Bull.* 154, **14,** 850 (February, 1913), which in turn is obtained from U. S. Government Specifications.

(2) The specifications referred to above are as follows: The pitch shall be straight-run residue obtained from the distillation of coal tar and shall meet the following requirements:

Melting point: 135–155° F.

Matter insoluble in benzol: 15–35%.

Sp. gr. at 60° F.: 1.25–1.35.

Evaporation loss, 7 hours at 325° F.: Maximum 9% for pitch of 145–155° F. m.p., and 11% for pitch of 135–145° m.p.

Sp. gr. of distillate to 670° F.: Minimum 1.07, determined at 140° F. as compared with water at 140° F.

BITUMINOUS AND ASPHALTIC ROAD BINDERS

General.—Asphalt road binders are generally bought by specification which prescribes the method of testing. Unless otherwise specified, however, the following procedures should be employed:

Water.—Weigh out approximately 10 grams of material on a filter paper, place the whole in a 300-cc. Erlenmeyer flask and

determine the water by the Xylol Method, as described on page 358.

Specific Gravity.—Determine the sp. gr. at 25°/25° C. by one of the following methods, depending upon the consistency of the sample.

Hydrometer Method (for Thin, Fluid Materials).—Bring the material to 25° C. in a hydrometer cylinder, place the hydrometer in it, and when it comes to rest, take the reading. In case the hydrometer sinks slowly, give it sufficient time to come to a definite resting point. Check this point by raising the hydrometer and letting it sink a second time. Never push the hydrometer below the point at which it naturally comes to rest until the last reading has been taken. Then push below the reading for a distance of 3 or 4 small scale divisions, whereupon it should immediately begin to rise. If it fails to do so, the material is too viscous for the hydrometer method.

The direct sp. gr. reading thus obtained is based on water at 15.5° C. as unity. To correct to water at 25° C. multiply by 1.002.

Pycnometer Method (for Viscous and Semisolid Materials).—Use a special pycnometer of the Hubbard type. First weigh the clean, dry pycnometer empty. Call this A. Fill with freshly boiled distilled water at 25° C. and again weigh. Call this B. Bring the sample to a fluid condition with the least possible heating and pour into the dry pycnometer, which may also be warmed, and fill $\frac{1}{2}$–$\frac{2}{3}$ full without allowing the material to touch the sides of the tube above the desired level. Cool to room temperature and weigh with the stopper. Call this C. Then pour in distilled water at 25° C. until the pycnometer is full. Insert the stopper and cool the whole to 25° C. by immersing completely for $\frac{1}{2}$ hour in a beaker of distilled water at this temperature. Remove all surplus moisture with a soft cloth and weigh. Call this D. Calculate the sp. gr. of the material by the following formula:

$$\text{Sp. gr. at } \frac{25°\text{C.}}{25°\text{C.}} = \frac{C-A}{(B-A)-(D-C)}.$$

Results by this method should be accurate to 0.002.

NOTE.—The sp. gr. of fluid material may be determined in the ordinary manner by completely filling the pycnometer with the material and dividing the weight of material taken by that of an equal volume of water.

DISPLACEMENT METHOD (FOR HARD, SOLID MATERIALS).—For materials which are hard enough to be broken and handled in fragments at room temperature, weigh a small piece suspended by means of a silk thread from the hook on the balance arm about 1.5 inches above the pan. Call this weight A. Then weigh immersed in water at 25° C. by placing a beaker about $\frac{2}{3}$ full of water on a support over the balance pan, but not touching it. Call this weight B. Calculate from the formula:

$$\text{Sp. gr.} = \frac{A}{A-B}.$$

Penetration Test.—Determine the penetration with a standard No. 2 Roberts needle, acting for 5 seconds under a total load of 100 grams, the temperature of the material being at 77° F., and report results in terms of hundredths of a centimeter, avoiding decimals.

APPARATUS.—The standard needle is made from round, polished, annealed steel drilling rod, diameter 0.0405–0.0410 inch. The rod is tapered to a sharp point at one end with the taper extending back 0.25 inch. The finished needle is 1.75–2.00 inches long and exactly 0.040 inch in diameter.*

The container for holding the material is a flat-bottom cylindrical dish $2\frac{3}{16}$ inches in diameter and $1\frac{3}{8}$ inches deep (this requirement is fulfilled by American Can Company's Gill style 3-ounce ointment box, deep pattern).

The penetration apparatus consists of a standard needle inserted in a short brass rod, which in turn is held in the aluminum rod of the apparatus by a binding screw. The frame, aluminum rod and needle weigh 50 grams without any weight on the bottom of the frame. For test with a 100-gram load, put on the 50-gram weight.

PROCEDURE.—Warm the sample sufficiently to flow and pour it into the tin box to a depth of not less than $\frac{5}{8}$ inch. Transfer to a glass crystallizing dish or other suitable dish and

* American Society for Testing Materials Standard D5–21 requires that the point of the needle shall be blunted by grinding off to a truncated cone, the smaller base of which shall be from 0.14 to 0.16 mm. in diameter.

cover with as much water at 77° F. as convenient without spilling. Let cool ½ hour at room temperature, protected from dust, then immerse in a large volume of water at exactly 77° F., and keep at that temperature 1½ hours. Place the dish containing the tin holder with the material on the shelf of the machine; make sure that the binding screw of the needle holder is tight and that the tin dish is firm so that no rocking motion can occur; lower the rod until the point of the needle almost touches the surface of the sample; finally very cautiously adjust until the needle point just comes in contact with the surface of the sample. This can best be seen by having a light so situated that upon looking through the sides of the glass cup, the needle will be reflected from the surface of the sample. After thus setting the needle, move the counterweight slowly until the foot of the rack rests on the head of the rod and take the reading of the dial. With one hand open the clamp by pressing the button and with the other hand start the chronometer. At the end of exactly 5 seconds release the clamp, lower the rack until it rests on top of the rod and again read the dial. The difference between the first and second readings in hundredths of a centimeter is the Penetration under the above conditions.*

Make at least 3 tests on points on the surface of the sample not less than ⅜ inch from the side of the container and not less than ⅜ inch apart. After each test return the sample and dish to the water bath at 77° F., and carefully wipe the needle *toward its point* with a clean, dry cloth to remove all adhering asphalt. The penetration reported shall be the average of at least 3 tests whose values do not differ by more than 4 points.

Notes.—(1) The point of the needle should be examined from time to time with a magnifying glass to see that it is not injured in any way. If it is found defective it may be removed by heating the brass rod and withdrawing with pliers. A new needle may then be inserted in the heated brass, and held firmly in place by a drop of soft solder.

(2) A cup suitable for holding the box containing the test material during penetration is conveniently made from a glass crystallizing dish 4 inches in diameter with straight sides about 2.5 inches high. Three right triangles, with right-angle sides 0.4 and 2 inches, respectively, are cut from $\frac{1}{16}$-inch

* After taking the reading, it is well to release the clamp again and note if the needle penetrates farther, to make sure that the point has not reached the bottom of the dish.

sheet metal, some solid bitumen is melted in the bottom of the dish, forming a layer about $\frac{1}{8}$ inch thick, into which the triangles are placed, resting on the side 2 inches long. Their apexes should meet the center with their short sides dividing the circumference of the dish into 3 equal parts. When the bitumen is hardened, the triangles give a firm support for the circular boxes and the possibility of any rocking motion, and consequent faulty results, is avoided.

Volatility.—Weigh out about 50 grams of the sample in a tin box $2\frac{3}{16}$ inches in diameter by about $1\frac{3}{8}$ inches deep (3-ounce Gill style ointment box, deep pattern), first carefully weighing the box; then adjust the weight of sample so that it does not vary more than 0.2 gram from 50. It may be necessary to warm some of the material slightly in order to handle it conveniently, after which it must be allowed to cool before determining the accurate weight.

Before making the test, the interior of the oven should show a temperature of 163° C. (325° F.). Heat the material in the oven for 5 hours, remove, cool in a desiccator and weigh. Calculate the percentage loss.

NOTES.—(1) For strictly accurate work the New York Testing Laboratory oven should be used. (See *U. S. Dept. Agr., Bull.* 314, 19.)

(2) In case it is not desired to determine the penetration of the residue, tests should be run on 20 grams of material in a tin container, 6 cm. in diameter by 2 cm. deep. In any case, the amount of material taken should be stated.

Float Test.—This test is always made on viscous and semi-solid refined tars and often on viscous and semi-solid petroleum and asphalt products, although, when penetration tests can be employed on the latter, the float test is not always considered necessary. For more fluid products make the test at 32° C.; for semisolid materials, at 50° C.; and in certain cases, on unusually hard materials, at 100° C.

The float apparatus consists of 2 parts, an aluminum float or saucer and a conical brass collar. Place the brass collar with the small end down on a brass plate previously amalgamated with Hg by rubbing it first with a dilute solution of mercuric chloride or nitrate and then with Hg. Heat a small quantity of the sample in a metal spoon until fluid, taking care that it suffers no appreciable loss by volatilization and that it is kept free from air bubbles. Pour into the collar in a thin stream until slightly

more than level with the top. Cool to room temperature and remove the surplus with a spatula which has been slightly heated. Place the collar and plate in ice water at about 5° C. for at least 15 minutes. Meanwhile place a 500-cc. cup or beaker, nearly filled with water, over a flame and heat to the test temperature. At the end of 15 minutes or more remove the collar with contents from the brass plate and screw it into the aluminum float, taking care to screw it in as far as it will go. Float the apparatus on the surface of the water, at the same instant starting a stop-watch. When water first breaks through the plug of bituminous material, stop the watch. The time in seconds between placing the apparatus on the water and when the water breaks through is the Float Test.

Flash Point.—Determine the flash point in the open cup tester as described on page 327.

Softening Point.—Bituminous materials have no true melting point. Any method of determining the "melting point" of these materials must be arbitrary. The 2 in most common use are the following:

Cube Method (Not applicable to pitches having a melting point above 77° C.).—First melt the material, if necessary, in a spoon by gentle application of heat until sufficiently fluid to pour readily, taking care that it suffers no appreciable loss by volatilization. Stir thoroughly, avoiding incorporating air bubbles in the mass. Then pour into a 0.5-inch brass cubical mold, which has been amalgamated with Hg, and which is placed on an amalgamated brass plate. The brass may be amalgamated by washing it first with a dilute solution of mercuric chloride or nitrate, after which the Hg is rubbed into the surface. By this means the bitumen is to a considerable extent prevented from sticking to the sides of the mold. The hot material should slightly more than fill the mold, and when cooled the excess should be cut off with a slightly heated spatula.

(*a*) *Pitches Having Softening Points between 43 and 77° C.*—Fill a 600-cc. low-form Griffin beaker to a depth of about 3.75 inches with freshly boiled distilled water at 15.5° C. Place the cube of pitch on an L-shaped right-angled hook made of No. 12 B. & S. gage copper wire. The foot of the L should be 1 inch long and should run through the center of the cube, so that one

edge of the cube, not its surface, is parallel to the bottom of the beaker and exactly 1 inch above it. The upper edge of the cube should be 2 inches below the surface of the water. Let it remain in the water for 15 minutes before applying heat to the beaker set on a wire gauze. Suspend the thermometer so that the bottom of the bulb is level with the bottom edge of the cube and within 0.25 inch of, but not touching, the cube.

Apply heat so that the temperature of the water is raised 5° C. (9° F.) per minute. The rate of rise must be uniform and should not be averaged over the period of test. The maximum permissible variation for any minute period after the first 3 minutes is ±0.5° C. (1° F.). If the rate of rise exceeds this limit, the test must be rejected.

The temperature recorded by the thermometer at the instant the pitch touches the bottom of the beaker is the softening point of the sample.

NOTES.—(1) The burner should be protected by a shield to avoid draft.

(2) The use of freshly boiled distilled water is essential to prevent air bubbles forming on the cube and retarding sinking.

(3) Rigid adherence to the prescribed rate of heating is absolutely essential for accuracy.

(4) A sheet of paper placed on the bottom of the beaker and weighted down will prevent the pitch from sticking to the glass and save considerable time and trouble in cleaning.

(5) The limit of accuracy of the test is ±0.5° C. (1° F.).

(6) The thermometer should be graduated from 0–80° C., preferably in $\frac{1}{5}$° divisions and the top of the mercury column at the time of reading should be above the surface of the water.

(*b*) *Pitches Having Softening Points below 43° C.*—Use the same method as given above, except that the water when placed in the beaker should be at a temperature of 4° C. instead of 15.5° C. Let the cube remain 15 minutes in this water before applying heat.

RING AND BALL METHOD.—*Apparatus.*—This consists of a brass ring exactly $\frac{5}{8}$ inch in diameter, $\frac{1}{4}$ inch deep, and with $\frac{3}{32}$ inch wall, suspended exactly 1 inch above the bottom of a beaker; a steel ball $\frac{3}{8}$ inch in diameter, weighing between 3.45 and 3.55 grams; a standardized thermometer of 0–80° C. range; and a low-form Griffin glass beaker of about 600-cc. capacity.

Procedure.—Carefully melt the sample, as in the Cube Method above, and fill the ring with excess of the material to be tested. During filling, rest the ring on amalgamated brass to prevent sticking. After cooling, remove the excess with a slightly heated spatula. Fill the beaker to a depth of about 3.25 inches with freshly boiled distilled water at 5° C.* Place the ball in the center of the upper surface of the material and suspend in water so that the lower surface of the filled ring is exactly 1 inch above the bottom of the beaker and the upper surface is 2 inches below the surface of the water. Let remain in the water for 15 minutes before applying heat. Suspend the thermometer so that the bottom of the bulb is level with the bottom of the ring and within 0.25 inch of, but not touching, the ring. Apply heat uniformly, so that the temperature of the water rises 5° C. (9° F.) per minute. The rate of rise must be uniform and is not to be averaged over the period of test. The maximum permissible variation for any minute period after the first three shall be $\pm 0.5°$ C. (1° F.). Reject any tests where the rate of rise exceeds these limits. The temperature recorded by the thermometer at the instant the sample touches the bottom of the beaker is its softening point (see notes under Cube Method above).

Total Bitumen (Soluble in Carbon Bisulfide.)—Prepare a Gooch crucible (the best size is 1.75 inches at the top, 1 inch deep, and 1.5 inches at the bottom) with an asbestos mat which will just show light through it. Suck dry, heat a few minutes in the oven, ignite over a Tirrill burner, cool in a desiccator and weigh. Place 1–10 grams of the sample, depending upon the amount of insoluble matter, in a 150-cc. Erlenmeyer flask, which has been previously weighed, and weigh accurately; then pour 100 cc. of CS_2 into the flask in small portions with continual agitation until all lumps disappear and nothing adheres to the bottom. Cork and set aside for 15 minutes or longer. Decant the CS_2 solution very carefully through the asbestos in the weighed Gooch crucible without suction, with care not to stir up any

* For materials having a softening point above 80° C. use glycerine instead of water, and have the starting point of the bath at 32° C., using a thermometer of 30–160° C. range. In this case the ring apparatus is placed off the center of the beaker and the burner placed midway between the center and the edge of the beaker away from the specimen.

precipitate. At the first sign of any sediment coming over, stop the decantation, and let the filter drain. Wash a small amount of CS_2 down the sides of the flask, bring the precipitate upon the mat and remove all adhering matter from the flask to the crucible with a policeman which is not attacked by CS_2. Wash the contents of the crucible with CS_2 until the washings are colorless. Apply suction until practically no odor of CS_2 remains in the crucible. Clean the outside of the crucible with a soft cloth moistened with a little CS_2. Dry at 100° C. for about 20 minutes, cool in a desiccator and weigh. (If any appreciable amount of insoluble matter adheres to the flask, it should also be dried and weighed and any increase over the original weight added to that of the insoluble matter in the crucible.)

The total weight of insoluble material may include both organic and mineral matter. Ignite at a red heat until no incandescent particles remain. Cool and weigh the mineral matter. Report the difference between 100% and the total percentage of material insoluble in CS_2 as Total Bitumen. Also report the percentage of mineral matter as Ash.

NOTES.—(1) In certain natural asphalts it is practically impossible to retain all finely divided mineral matter on an asbestos mat. It is, therefore, generally more accurate to obtain the result for total mineral matter by direct ignition of 1 gram in a platinum crucible, or to use the result for ash obtained in the fixed carbon test. Then determine the total bitumen by deducting from 100% the sum of the percentages of total mineral matter and of organic insoluble matter. If the presence of carbonate mineral is suspected, the percentage of mineral matter may be most accurately determined by treating the ash from the fixed carbon determination with a few drops of ammonium carbonate solution, drying at 100° C., then heating for a few minutes at dull red heat, cooling and weighing again.

(2) When unusual difficulty in filtering is experienced, it is necessary to let stand much longer than 15 minutes. In such cases it is preferable to proceed as follows:

Weigh 2–15 grams (depending on richness in bitumen) into a 150-cc. Erlenmeyer flask, which has been previously weighed, and treat with 100 cc. of CS_2. Cork the flask loosely and shake from time to time, until practically all large particles have been broken up. Set aside undisturbed for 48 hours. Decant the solution into a similar flask that has been previously weighed, as much of the solvent being poured off as possible without disturbing the residue. Treat the first flask again with fresh CS_2, and shake as before. Put away with the second flask undisturbed for 48 hours.

At the end of this time carefully decant off the contents of the 2 flasks upon a weighed Gooch crucible fitted with an asbestos filter, the contents of

the second flask being passed through the filter first. The asbestos filter should be made of ignited long-fiber amphibole, packed in the bottom of the Gooch crucible to a depth of not over $\frac{1}{8}$ inch. After passing the contents of both flasks through the filter, shake the 2 residues with more fresh CS_2 and set aside for 24 hours without disturbing, or until good subsidation has taken place. Again decant the solvent off upon the filter. Continue this washing until the filtrate or washings are practically colorless.

Dry the crucible and both flasks at 125° C. and weigh. Evaporate the filtrate containing the bitumen (either spontaneously at room temperature or by distillation from a hot water bath), burn the bituminous residue, and add the weight of ash thus obtained to that of the residue in the 2 flasks and crucible. The sum of these weights deducted from the weight of substance taken gives the weight of bitumen extracted.

(3) In the analysis of tars the insoluble organic matter is commonly known and reported as Free Carbon.

Bitumen Insoluble in 86° Naphtha.—This determination is made in the same general way as the Total Bitumen, using instead of CS_2 100 cc. of naphtha, at least 85% of which distills between 35 and 65° C. It is advisable to heat the sample after it has been weighed into the flask and let it cool in a thin layer around the lower part. Not more than $\frac{1}{2}$ the total amount of naphtha required should be used until the sample is entirely broken up; then add the remainder, swirl the flask, mix thoroughly, cork and set aside for 30 minutes or more. In making the filtration use the utmost care to avoid stirring up any of the precipitate, and make the first decantation as complete as possible. Suction may be applied when filtration by gravity almost ceases, but should be used sparingly as it tends to clog the filter. The material on the felt should never be allowed to run dry until washing is completed as shown by a colorless filtrate. When considerable insoluble matter adheres to the flask, make no attempt to remove it completely, merely wash until free from soluble matter and dry the flask (after removing naphtha) for about 1 hour at 100° C., after which cool and weigh. The percentage of bitumen insoluble in naphtha is reported upon the basis of the total bitumen taken as 100%.

NOTE.—The difference between the amounts insoluble in CS_2 and in naphtha is the bitumen insoluble in naphtha. If, for instance, the insoluble in CS_2 is 1% and the total insoluble in naphtha is 10.9%, the calculation of percentage of bitumen insoluble in naphtha is as follows:

$$\frac{\text{Bit. insol. in naphtha}}{\text{Total bitumen}} = \frac{10.9-1}{100-1} = \frac{9.9}{99} = 10\%.$$

Fixed Carbon and Ash.—Determine fixed carbon and ash on 1 gram as in Coal (pp. 214–215). (See also under Total Bitumen above.)

Distillation.—From the sp. gr. of the material calculate the weight of 100 cc. and pour this amount into a tared 250-cc. Engler distillation flask, after warming in a tin cup, if necessary, to make it sufficiently fluid. For the procedure in distilling and apparatus used see page 802. Report results both as percentages by weight and by volume, or as required.

Ductility.—Form a briquette of the sample by pouring the molten material into a briquette mould. The dimensions of the briquette shall be: 1 cm. (0.394 inch) in thickness throughout its entire length; distance between clips or end pieces, 3 cm.; width of asphalt cement section at mouth of clips, 2 cm.; width at minimum cross-section, half-way between clips, 1 cm. The center pieces are removable, the briquette mold being held together during molding with a clamp or wire.

The molding of the briquette is to be done as follows: The 2 center sections must be well amalgamated to prevent the sample from adhering to them. Then place the briquette mold on a freshly amalgamated brass plate. Pour the sample to be tested, while in a molten state, into the mold, adding a slight excess to allow for shrinkage on cooling. When the material in the mold is nearly cool, cut off the briquette level with a warm knife or spatula. When thoroughly cooled to the proper temperature, remove the clamp and the 2 side pieces, leaving the briquette held at each end by the ends of the mold, which now play the part of clips. Keep the briquette in water for 30 minutes at 4° C. (39° F.) or 25° C. (77° F.) before testing, dependent on the temperature at which the ductility is desired. Place the briquette with clips attached in the ductility test machine, filled with water at one of the above temperatures to a sufficient height to cover the briquette not less than 5 cm. (1.97 in.). The machine consists of a rectangular water-tight box, having a movable block working on a worm gear from left to right. The left clip is held rigid by placing its ring over a short metal peg provided for this purpose; the right clip is placed over a similar rigid peg on the movable block. The latter is provided with a pointer which moves along a centimeter scale. Before starting the test,

adjust the centimeter scale with the pointer at zero. Then apply power by the worm gear, pulling from left to right at a uniform rate of 5 cm. per minute. The distance in centimeters registered by the pointer on the scale at the time of rupture of the thread of asphalt material is taken as the ductility of the material.

Paraffin Scale.—The determination of paraffin scale is seldom required. The procedure is described in *U. S. Department of Agr., Bull.* 314, page 32.

Petroleum or Asphalt Products in Tar.—Take fractions of the distillation from 270–300° C., from 300–350° C., and from 350–375° C., respectively. Stir each fraction separately and, if necessary, warm to dissolve any solids.

To 4 cc. of each fraction in tubes graduated to 0.1 cc. add 6 cc. of dimethyl sulfate. Shake well and let stand 30 minutes. Read off the volume of any oil separating on top of the liquid. This is due to asphalt or petroleum products. Calculate the volume percentage in each fraction and report as follows:

Fractions °C.	Per Cent Distillate	Per Cent Distillate Insoluble in Dimethyl Sulfate
270–300	.....	.....
300–350	.....	.....
350–375	.....	.....

The test is mainly qualitative but will indicate as little as 3% of petroleum or asphalt products in tar.

References.—Sp. Gr., Flash Point, Float Test, Penetration, Melting Point (Cube Method) and Bitumen: *U. S. Dept. Agr., Bull.* 314.

Melting Point: American Society for Testing Materials Standard D36–24 (Ring and Ball Method) and D61–24 (Cube Method).

Volatility: *U. S. Dept. Agr., Bull.* 314, 19, and *Bull.* 555, 36.

Ductility and Paraffin: *Proc. Am. Soc. Civil Eng.*, 3047 and 3049 (1914).

See also articles by J. M. Weiss in *J. Ind. Eng. Chem.*, 1918, "Methods of Analysis used in the Coal Tar Industry."

CRUDE COAL-TAR AND WATER-GAS TAR

General.—The analysis of crude coal- and water-gas tars generally involves the following determinations: Specific gravity, free carbon, water, fractional distillation, and tar acids.

Sampling.—Tar is best sampled when being unloaded from the tank car or barge. A pet-cock, with a nipple projecting about one-third of its diameter, should be placed in the pipe line and a continuous stream of tar drawn off into a barrel during the time of unloading. The pet-cock should be so regulated that the sample will represent approximately 0.1% of the shipment. The tar may then be stirred up and a sample taken from the barrel. Samples of tar should be placed in heavy clear bottles or screw-top tin cans.

When necessary to sample from storage tanks, or wells, it should be done by means of a "thief." This is particularly necessary when different shipments of tar of widely different gravities have been run into the same tank. A simple and efficient apparatus may be made from a piece of 2-in. pipe provided with a lever handle-cock. This may be closed by means of a small iron rod. By cutting away part of the cock and half of the plug, an opening nearly as large as the interior of the pipe is produced. In taking the sample, the cock is opened and the "thief" lowered slowly to the bottom of the tank, well, or car, the "thief" having previously been rinsed with the liquid to be sampled. The cock is then closed, the "thief" is withdrawn, and the sample run into a bottle. This operation is repeated until a sample of about 1 gallon is obtained, after which the contents should be thoroughly mixed and a portion taken to serve as a smaller sample for analysis.

It should be noted that this method cannot be used with horizontal cylindrical tanks.

In the case of tar where there is always a certain amount of water or ammoniacal liquor floating on the surface, it seems best to attempt to locate the level of the water or liquor, taking a sample at this point, and then sample a lower portion of the tar which is reasonably free from water, and by calculation, estimate the total quantity of water present.

Specific Gravity.—The sp. gr. of thin tar, such as water-gas tar, free from water, may be determined by the Westphal balance. The measurements should be made at 25° C. where possible. Take the reading with the Westphal balance at 25° C. Balance the plummet in distilled water also at 25° C. and take the reading. Divide the first reading by the second. This is the sp. gr. of the

material at 25° C. If it is not possible to take readings at 25° C., balance the plummet in the sample and also in distilled water at the temperature $t°$ and correct the sp. gr. to 25° C. as follows: If $t°$ is greater than 25°, then

$$\text{Sp. gr. at } 25° \text{ C.} = \text{sp. gr. at } t° \text{ C.} + 0.00068\ (t-25).$$

In case $t°$ is less than 25°, then

$$\text{Sp. gr. at } 25° \text{ C.} = \text{sp. gr. at } t° \text{ C.} - 0.00068\ (25-t).$$

A hydrometer may be used in place of the Westphal balance. Since hydrometers are standardized for water at 15.5° C., the hydrometer reading in the tar at 25° C. should be multiplied by 1.002 to bring it to the basis of $H_2O = 1$ at 25° C.

For accurate work and for thick tars the modified Hubbard's sp. gr. bottle should be used. In using this bottle the following weights are necessary in the order given:

A = Weight of empty bottle;

B = Weight of bottle filled with water to the mark at 25° C.;

and C = Weight of bottle filled with tar at 25° C.;

then sp. gr. of tar at $\frac{25° \text{ C.}}{25° \text{ C.}} = \frac{C-A}{B-A}$.

Note.—The Hubbard method is not accurate for tar containing water. In such case the tar should be dehydrated, as described below under Distillation, and the sp. gr. determined on the dehydrated tar. The sp. gr. of the original tar may be calculated as follows:

Let A = Sp. gr. of dehydrated tar;

B = Percentage of water expressed as decimal;

and X = Sp. gr. of original tar;

then $X = B + A\ (1-B)$.

Moisture.—For most purposes the Xylol Method is suitable, as described on page 358.

In cases of dispute, however, use the method described in the "Gas Chemists' Hand Book," page 191 (1916), as follows: Measure 50 cc. of coal-tar naphtha or light oil (which must be tested to determine that it is free from water whenever a new supply is required) in a 250-cc. graduated cylinder. Add 200 cc. of the tar, transfer the contents of the cylinder to a copper still (see below under Distillation) and wash the cylinder with 50–75 cc. more of naphtha, adding the washing to the contents of the still.

Attach the lid and clamp, using a paper gasket. Distill through a still head, connected to a condenser, and collect the distillate in a separatory funnel having a graduated stem to which 15–20 cc. of benzene have been previously added. Apply heat to the still by means of the ring burner and distill until the temperature as indicated by the thermometer has reached 205° C. The bulb of the thermometer must be opposite the side neck of the still head. The reading of the volume of water is made after twirling the funnel and letting the water settle for a few minutes. Calculate the percentage by volume.

Free Carbon.—For accurate work the tar should be dried before testing and after drying passed hot through a 30-mesh sieve to remove foreign substances. This ordinarily, however, is not necessary as such foreign substances could easily be detected during analysis.

From materials with 5% or more carbon take about 5 grams, with lesser percentages take 10 grams approximately. Weigh out the sample in a 100-cc. beaker and digest with about 5 cc. of pure toluene on the steam bath for not over 30 minutes. If the solution is kept hot and constantly stirred, digestion can be completed very rapidly.

Weigh in a weighing bottle a filter cup prepared as described below and place in a carbon filter tube over a beaker or flask. Decant the toluene tar mixture through the thimble and wash with hot toluene until clean. After transferring all the material from the beaker, wash once with hot pure benzene, drain, cover with a cap of filter paper and extract with benzene in an extractor of the Cottle or Rubber Insulation Committee type as used in rubber analysis (see Fig. 39, p. 752). Continue extraction until the descending benzene is colorless; remove the thimble, discard the cap, dry at 105° C. and weigh in the same weighing bottle as originally used. The residue is carbon. Report the result as Free Carbon (Toluene-benzene Method).

Notes.—(1) If the carbon is contaminated by dirt, ignite in a crucible and weigh the inorganic residue. Subtract this from the original weight of residue.

(2) *Filter cups:* The filter cups or thimbles are made of 15-cm. hardened filter paper. To make a cup, take 2 circles and cut one down to a diameter of about 14 cm. Use a round stick about 1 inch in diameter as a form. Place the stick in the center of the circles of filter paper, the smaller inside;

then fold the papers symmetrically round the stick to form a cup of about 2.5 inches in length. After making the cups, soak them in benzene to remove any grease due to handling, drain, dry in a steam oven, and keep in a desiccator until used.

Distillation.—Sampling.—The sample as received must be thoroughly stirred and agitated, warming, if necessary, to insure complete mixture before the portion for analysis is removed.

Dehydration.—If the presence of water is suspected or known, dehydrate the material before distillation. Place about 300–400 cc. in a copper still (A. H. Thomas Co., Catalog No. 20416) provided with a distilling head connected with a water-cooled condenser. Use a ring burner, starting with a small flame at the top of the still, and gradually lowering, if necessary, until all water has been driven off and the thermometer reads 170° C. (The bulb of the thermometer should be opposite the side tube of the distilling head.) Collect the distillate in a 200-cc. separatory funnel with the tube cut off close to the stop-cock. When all water has been driven over and the distillate has separated clear, draw off the water and return the oils to the residue in the still. (If crystals separate, warm the mixture until they go into solution.) Let the contents of the still cool to below 100° C. before the oils are returned; stir well and mix with the residue.

Apparatus.—The apparatus consists of the following standard parts:

(*a*) *Flask.*—The distillation flask is a 250-cc. Engler distilling flask, of the following dimensions:

Diameter of bulb	8.0 cm.
Length of neck	15.0 cm.
Diameter of neck	1.7 cm.
Surface of material to lower side of tubulature	11.0 cm.
Length of tubulature	15.0 cm.
Diameter of tubulature	0.9 cm.
Angle of tubulature	75°

A variation of 3% from the above measurements is allowed.

(*b*) *Thermometer.*—The thermometer is of hardened glass, filled with inert gas under pressure and provided with an expansion chamber at the top; it reads from 0 to 400° C. or 450° C., is graduated in single degrees Centigrade, and has the following dimensions:

Diameter of stem	6.5–7.5 mm.	(approximately).
Length of thermometer	385 mm.	
Length from 0° to 400° marks	285–305 mm.	
Length of bulb	10–15 mm.	
Diameter of bulb	5 mm.	and not exceeding diameter of stem.
Distance from zero to bottom of bulb	25–35 mm.	

When the thermometer is taken at a temperature of 26° C. and plunged into a free flow of live steam, the meniscus must pass the 90° mark in not more than 6 seconds.

(*c*) *Condenser.*—The condenser tube has the following dimensions:

Length of tube	500 mm.
Width of tube	12–15 mm.
Width of adaptor end of tube	20–25 mm.

(*d*) *Stands.*—Two iron stands are required, one with a universal clamp for holding the condenser, and one with a light grip arm with a cork-lined clamp for holding the flask.

(*e*) *Burner and Shield.*—The Bunsen* burner must be provided with a tin shield 20 cm. long and 9 cm. diameter, having a small hole for observing the flame.

(*f*) *Cylinders.*—The cylinders used in collecting the distillate have a capacity of 25 cc., and are graduated to 0.1 cc.

Setting up Apparatus.—Connect the distilling flask containing the tar to the air condenser with a 1-hole stopper. Insert the thermometer through a 1-hole stopper in the top of the flask in such a way that the top of the bulb is opposite the middle of the side-arm opening of the flask. Have the burner so adjusted that the shield will completely protect the flame and also the bulb of the distilling flask.

Procedure.—Weigh exactly 100 cc. of the dehydrated material into the distilling flask, which has been previously weighed. Adjust the thermometer, shield, condenser, etc. Commence distillation, so regulating the rate that 1 cc. passes over every minute. Change the receiver as the mercury column just passes the fractionation point.

*Or Tirrill.

Report the temperature at which the first drop comes over and then report the percentage of each of the following fractions, both by weight and by volume:

(1) Up to 110° C.
(2) 110–170° C.
(3) 170–235° C.
(4) 235–270° C.
(5) 270–300° C.
(6) 300–315° C.
(7) 315–355° C.
(8) Residue above 355° C.

The residue is determined by cooling the flask after distillation and weighing it. During the distillation the condenser tube should be warmed when necessary to prevent deposition of any sublimate.

NOTE.—This method is based on standard method D20–18 of the American Society for Testing Materials.

Tar Acids.—Distill a known volume of the tar up to 315° C. For each 100 cc. of distillate add 40 cc. of an approximately 20% solution of NaOH. Warm slightly while stirring and place in a separatory funnel. Shake vigorously, let stand until the oil and NaOH solutions separate, and draw off the latter containing most of the tar acids. Make a second and third extraction, using 75% and 50% of the original volume of NaOH solution, respectively. Unite the 3 alkaline extracts in a 200-cc. graduated cylinder (see below) and acidify with dil. H_2SO_4. Let cool and read the volume of tar acids. From the amount of tar taken calculate the percentage by volume of tar acids in the original tar.

NOTE.—The cylinder or separatory funnel should be of special form with a stop-cock and graduated stem so that the tar acids may be drawn down in the graduated portion and the volume accurately determined.

Sulfur.—See page 252.

Road Tars.—The examination of road tars is usually made to conform to particular specifications which describe the method. If methods are not specified, follow the procedures on page 787.

REFERENCES.—"Gas Chemists' Handbook," 1916; Am. Soc. for Testing Materials: "Triennial Standards," 951 (1924).

SPENT OXIDE

General.—The material used for the removal of H_2S from illuminating gas is known under various names, such as oxide, iron oxide, iron mass, iron sponge, etc. After it has been in use for some time, it is generally referred to as Spent Oxide. It consists of wood shavings mixed with hydrated ferric oxide. The action of H_2S on this material is probably represented by the following equations:

$$Fe_2O_3 \cdot H_2O + 3H_2S = Fe_2S_3 + 4H_2O,$$

and

$$Fe_2O_3 \cdot H_2O + 3H_2S = 2FeS + S + 4H_2O.$$

After the material has become "foul," it is revivified or reoxidized by exposure to air. The reactions here are probably as follows:

$$2Fe_2S_3 + 3O_2 = 2Fe_2O_3 + 6S,$$

and

$$4FeS + 3O_2 = 2Fe_2O_3 + 4S.$$

There are also present Prussian blue and other cyanogen and carbonyl products. In selling the material for its cyanogen content, it is customary to calculate the latter in terms of crystallized potassium ferrocyanide, $K_4Fe(CN)_6 \cdot 3H_2O$.

Moisture.—When the material arrives in the laboratory, it is usually in such condition, due to moisture and tarry matter, that it must be dried before grinding. Mix the sample thoroughly and weigh out 100 grams (or more if possible) into a rectangular tin dish and dry to constant weight, keeping the temperature as nearly as possible between 90 and 95° C. When ferrocyanide is to be determined, dry for 9 hours at 50–60° C. It is unsafe to hasten drying by raising the heat, as this will volatilize some of the free S, and may decompose Prussian blue.

Preparation of Sample.—Grind the dried sample in an ordinary coffee mill, repeating the grinding until the material is as fine as possible. By bringing the grinding surfaces closer together each time, it is possible to reduce the mass almost to a powder. For accurate work, determine the residual moisture in the ground sample and make such corrections as are necessary in figures obtained in the subsequent analysis to bring them to the basis of the original material.

NOTE.—In grinding it is very essential, in case ferrocyanide is to be determined, that the temperature should not get above 50–60° C., as excessive heating will cause loss of cyanogen.

Free Sulfur.—Since, for commercial purposes, S combined as iron sulfide may be considered in the same category as free S, the analysis is shortened by determining these two forms of S together. The method is based on the fact that free S is dissolved by CS_2. Since the latter, however, will dissolve only *free* S, some of the sample should be spread out and exposed to air for "revivification" before extracting. The sample must also be dry, since moisture interferes with the extraction.

Weigh 5 grams of the ground dry material on a watch glass and heat in a water oven at not over 95° C. to constant weight in order to remove the last traces of moisture. Transfer to a Soxhlet thimble and extract with recently distilled CS_2* until no further material is extracted, collecting the extract in a weighed flask. Distill off the CS_2 on the water bath through a Liebig condenser. Dry the residue to constant weight at not over 100° C. The weight gives the amount of tar and free S.

Add to the flask 50 cc. of fuming HNO_3, evaporate on the hot plate or sand bath to half its volume, then add, *little by little*, 3 grams of $KClO_3$, and evaporate to dryness. Bake on the hot plate for $\frac{1}{2}$ hour, cool and add 30 cc. of dil. HCl (1 : 1). Boil, filter and wash with hot water. Heat the filtrate to boiling and add slowly a boiling 10% solution of $BaCl_2$ in excess. Boil for $\frac{1}{2}$ hour, or let stand overnight; filter hot, wash, ignite and weigh the $BaSO_4$ in the usual way. Calculate the weight to sulfur.

CALCULATION.—$BaSO_4 \times 0.1373 = S$.

NOTES.—(1) The CS_2 extraction is a slow one; the length of time required depends upon the percentage of S and the amount of tar. Usually 30 hours will be sufficient.

(2) The free S in spent oxides may run from a few per cent to as high as 55 or 60%.

Tar.—The weight of S subtracted from the total weight of CS_2 extract gives the weight of tar.

* CS_2 is very inflammable and in the gaseous state, when mixed with a certain percentage of air, is highly explosive. The extraction apparatus should never be disconnected until it has cooled down to room temperature.

Combined Sulfur.—If it is desired to determine the combined S, this may be done on the residue from the CS_2 extraction, after making sure that all CS_2 has been expelled. After oxidizing with fuming HNO_3, as described under Free Sulfur, and filtering, dry the undecomposed material on the filter paper and fuse it with equal parts of Na_2CO_3 and $NaNO_3$. Disintegrate with hot water, filter and wash. Dilute the filtrate to 250 cc. and acidulate with HCl Boil off CO_2 and precipitate hot with excess of $BaCl_2$ solution. Add the S thus found to the S found by the HNO_3 treatment. The sum gives combined S.

Potassium Ferrocyanide (Modified Knublauch Method).—Moisture.—Dry 30 grams of the material for 9 hours at 50–60° C.

Extraction of Prussian Blue.—Grind the dried oxide until it all passes an 80-mesh sieve, taking care to *avoid heating.* Introduce 10 grams of this fine material into a 250-cc. volumetric flask. Add 50 cc. of 10% KOH solution and let stand 15–16 hours at room temperature, shaking frequently. Then make up to 250 cc. and add 5 cc. more to compensate for the volume of the oxide. Shake vigorously and filter through a dry filter. Some free S may come through the filter paper, but most of this can be removed by refiltering through the same paper. What remains will do no harm.

Pipette out 100 cc. of this filtrate and let it run slowly into 50 cc. of a boiling solution of $FeCl_3$.* Boil the mixture a few minutes to complete the precipitation of the Prussian blue. After this settles a little, filter and wash with boiling water until the washings are free from acid. Transfer the blue, together with the filter paper, into a 400-cc. beaker and add 25 cc. of 10% KOH solution. After complete decomposition, transfer to a 250-cc. volumetric flask and make up to the mark. Shake and filter through a dry filter. Use 100 cc. of this filtrate for titration.

Preparation of Solutions.—*Zinc Sulfate Solution.*—Weigh out 10 grams of $ZnSO_4 \cdot 7H_2O$, dissolve in water, add 10 cc. of conc. H_2SO_4 and dilute to 1 liter in a volumetric flask.

Potassium Ferrocyanide Solution.—Weigh out exactly 5 grams of $K_4Fe(CN)_6 \cdot 3H_2O$. This should be chemically pure and

* Dissolve 60 grams of $FeCl_3$ crystals in water, add 100 cc. of conc. HCl and dilute to 1 liter.

contain the full amount of water of crystallization. If the latter is more or less, a correction must be made. Dissolve in water and make up to 250 cc.

Standardization of $ZnSO_4$ Solution.—Measure out 25 cc. of the ferrocyanide solution into a beaker. Add about 50 cc. of water and 10 cc. of 10% H_2SO_4. Titrate with the $ZnSO_4$ solution from a burette.

As an outside indicator use a 3% solution of ferric alum on Schleicher and Schull's drop-reaction paper No. 601.* Place 1 drop of ferric alum solution on the paper and let it spread as far as it will. Place a drop of the solution being titrated so that its extreme edge, after spreading, just meets the edge of the ferric alum drop. If the two over-run, faulty results will follow. The end-point of the titration is reached when a blue coloration at the point where the 2 drops meet does not appear for a space of 1 minute. Questionable end-points may be detected by holding the test paper so that strong sunlight passes through it. The faintest trace of blue is readily detected in this way. Titrations should not be attempted by artificial light or on dull, cloudy days. At least 3 titrations should be made, the first to find the approximate amount of $ZnSO_4$ solution required. The second and third titrations should check each other closely.

From the titration calculate the value of 1 cc. of $ZnSO_4$ solution in terms of $K_4Fe(CN)_6 \cdot 3H_2O$.

Titration of Prepared Solution.—Place in a beaker 100 cc. of the solution prepared as described under Extraction of Prussian Blue. Add a drop or two of methyl orange indicator, neutralize with 10% H_2SO_4 and then add 10 cc. excess. Titrate with standard $ZnSO_4$ solution, using ferric alum as outside indicator, exactly as in the standardization. From the strength of the $ZnSO_4$ solution calculate the percentage of $K_4Fe(CN)_6 \cdot 3H_2O$ both in the sample as received and on the dry basis.

* This is the only paper which we have found satisfactory. Other papers, such as Whatman's, give a blue color directly with the reagent. They can be made satisfactory, however, by treatment with very dil. HCl as follows: Place the entire sheet in a large beaker and cover it with HCl of between 2 and 5% strength. Boil gently or digest on the steam bath for about ½ hour. Wash free from acid; then continue washing until free from Cl. Dry in the air protected from chemical fumes.

NOTE.—The entire success of the method depends upon obtaining the correct end-point. Titrations must be carried out in strong sunlight, never by artificial light.

REFERENCES.—*Proc. Am. Gas Inst.*, **7**, 761; R. H. Royle: "Chemistry of Gas Manufacture," 174; "Gas Chemists' Handbook."

MORTAR AND CONCRETE

General.—Structural concrete consists of sand, gravel and cement. In mortar the gravel (large aggregate) is omitted. In some mortars also lime is used. These lime mortars generally contain an amount of lime about equal to the amount of cement. The setting of cement is a process of hydration; therefore, in order to obtain the composition of the original material, the analysis must be made on the sample after ignition.

Gravel.—Any stone or coarse aggregate which will not pass through a sieve with $\frac{1}{4}$-inch openings* is considered gravel; material finer than $\frac{1}{4}$-inch is considered sand. If the composition contains gravel, the whole sample should be weighed and disintegrated with a hammer or mortar and pestle, taking care not to crush or break the stone or sand particles. Knock off the cement from the large particles. Then determine the percentage of the whole sample which will not go through a $\frac{1}{4}$-inch sieve and report as Gravel.

Thoroughly mix the finer portion, and weigh out a known quantity, generally 10–50 grams, depending upon the size of the particles. Ignite and determine loss on ignition. Then proceed with the determinations of Sand, etc., as below, beginning "Treat with a considerable volume of dil. HCl."

Sand.—If the original material is fine and appears to be fairly uniform (as in the case of mortars and surfacings), crush gently and mix thoroughly. Ignite a portion and weigh out 5–10 grams of the ignited sample. Treat with a considerable volume of dil. HCl (not stronger than 1:10) and warm on the steam bath. Decant the liquid through a filter into a volumetric flask. (If CaO and MgO are not to be determined, discard the filtrate; see Note 2.) Add a second portion of dil. HCl, again warm and decant. Continue this until all soluble matter has been removed. Wash with hot water, finally transferring all the residue to the

* This is not a 4-mesh sieve, *i.e.*, a sieve with 4 openings to the inch.

filter. Ignite in a weighed crucible, cool in a desiccator and weigh. This gives the Sand.

NOTES.—(1) Some of the SiO_2 from the cement may be thrown out of solution as silicic acid. The amount, however, is small if dilute acid is used and is largely compensated by the small amount of iron and alumina which is dissolved from the sand.

(2) In case of concrete and mortars free from added lime or limestone, it is sufficiently accurate to consider the rest of the material as cement. From the loss on ignition of the sand plus cement calculate what the weight of the entire sample would have been after ignition. On this weight figure the percentages of gravel and sand, and take cement "by difference."

Total Lime and Magnesia.—If the material contains added lime or limestone, make the filtrate up to volume and take an aliquot representing about 2 grams of the original ignited portion. Make slightly alkaline with NH_4OH, boil, and filter out any Fe and Al hydroxides. To the hot filtrate add an excess of $(NH_4)_2C_2O_4$ solution. Heat to boiling and let stand until the precipitate settles clear. Filter, wash with hot water and ignite over a blast lamp in a weighed platinum crucible. Cool in a desiccator and weigh as CaO. (The CaC_2O_4 may also be titrated with 0.1 N $KMnO_4$ in the usual way instead of igniting.)

Test a little of the filtrate from the CaO determination for MgO. If any appreciable amount is present it must be determined as follows: Return to the main filtrate the portion of the filtrate on which the qualitative test was made. Make slightly acid with HCl and evaporate until crystallization begins. Cool and dilute sufficiently to redissolve any crystals. Add a considerable excess of a solution of Na or NH_4 phosphate and then make strongly ammoniacal. Let stand overnight (or cool in ice water and stir for about $\frac{1}{2}$ hour). Filter through a weighed Gooch crucible, wash with a mixture of 1 part of dil. NH_4OH (1 : 1), 1 part of alcohol, and 3 parts of water. Ignite very gently at first and finally blast thoroughly. Cool in a desiccator and weigh as $Mg_2P_2O_7$. Calculate to MgO.

CALCULATION.—$Mg_2P_2O_7 \times 0.3621 = MgO$.

NOTE.—Since the entire procedure gives of necessity only approximate results, it is not necessary to make a double precipitation of the CaC_2O_4 before determining Mgo.

CALCULATIONS.—If the brand of cement is known, look up the amount of CaO it contains. If the brand is not known, assume

that it contains 62% CaO. Then, assuming that the ignited material consists entirely of sand, cement, and free lime (and MgO), and that the cement itself contains 62% CaO (+MgO), calculate the proportions in the sample as follows:

Subtract the percentage of sand and gravel from 100%. The difference is cement+CaO+MgO. (This is B below.)

Let A = Total CaO+MgO (found by analysis),
B = Cement+free CaO+free MgO,
and X = Cement;
then $B-X$ = Free (CaO+MgO),
and $A = B-X+0.62\,X$
$= B-0.38\,X$.
Or $0.38\,X = B-A$;
and $X = \frac{B-A}{0.38}$.

NOTE.—If high-calcium lime was used, there will be very little MgO present; but if dolomitic lime was used, there will be considerable MgO.

SAMPLING AND PHYSICAL TESTING OF PORTLAND CEMENT

General.—The following procedure is based on specification C 9-26 of the American Society for Testing Materials.* Portland cement is there defined as "the product obtained by finely pulverizing clinker produced by calcining to incipient fusion an intimate and properly proportioned mixture of argillaceous and calcareous materials, with no additions subsequent to calcination excepting water and calcined or uncalcined gypsum."

Portland cement is usually purchased on the basis of physical tests only, and unless expressly requested, no chemical tests are necessary.

Specifications for Physical Requirements.—The standard specifications of the American Society for Testing Materials were revised in 1926 to become effective January 1, 1927. Unless otherwise instructed, cement is to be tested according to the revised specifications. As some engineers, however, request

* As a supplement to this specification the American Society for Testing Materials has issued a "Manual of Cement Testing," which is a reprint from its *Proc.*, **25**, I (1925). Anyone who has occasion to do commercial cement testing should read this manual, which also contains a good bibliography on Portland cement.

tests according to the old specifications, both requirements are given below:

	Old Specifications		New Specifications	
	Maximum	Minimum	Maximum	Minimum
Specific gravity:				
Ordinary Portland cement	.....	3.10	.....	3.10
White Portland cement	.....	.....	.....	3.07
Fineness:				
Residue on 100-mesh sieve	8 %	.....	.....	.....
Residue on 200-mesh sieve	25 %	.....	22 %	.....
Initial set:				
Gillmore needle	.....	.....	.....	60 minutes
Vicat needle	.....	30 minutes	.....	45 minutes
Final set:				
Gillmore needle	.....	.....	10 hours	.....
Vicat needle	10 hours	1 hour	10 hours	.....
Tensile strength (neat)				
24 hours	.....	175 pounds	.....	.....
7 days	.....	500 pounds	.....	.....
28 days	.....	600 pounds	.....	.....
Tensile strength (1 : 3 mortar)				
7 days	.....	200 pounds	.....	225 pounds
28 days	.....	275 pounds	.....	325 pounds

A pat of neat cement shall remain firm and hard and show no signs of distortion, cracking, checking, or disintegration in the steam test for Soundness described below.

A bag of cement shall contain 94 pounds net; a barrel, 376 pounds net.

NOTES.—(1) If the sample under test falls below the sp. gr. requirement, a second test may be made on an ignited sample. The sp. gr. test is not required by the revised specifications unless specifically requested.

(2) The average tensile strength of standard mortar at 28 days shall always be higher than the strength at 7 days.

(3) At least 10 days from the time of sampling shall be allowed for the completion of the 7-day test and 31 days for the 28-day test.

(4) The Gillmore needle is used on setting tests in this laboratory unless otherwise requested.

Rejection.—Cement may be rejected if it fails to meet any of the requirements of the specifications. It shall not be rejected on account of failure to meet the fineness requirement if, upon retest after drying at 100° C. for 1 hour, it meets this requirement. Cement failing to meet the soundness test in steam may be

accepted if it passes a retest, using a new sample, at any time within 28 days thereafter.

Packages varying more than 5% from the specified weight may be rejected; and if the average weight of 50 packages taken at random from any shipment is less than that specified, the entire shipment may be rejected.

Sampling.—Tests may be made on individual or composite samples. Each test sample should weigh at least 8 pounds. Samples should preferably be shipped and stored in air-tight containers.

(*a*) INDIVIDUAL SAMPLE.—If sampled in cars, take 1 test sample from each 50 barrels or fraction thereof. If sampled in bins, take 1 sample from each 100 barrels.

(*b*) COMPOSITE SAMPLE.—If sampled in cars, take 1 samplerful from 1 of each 40 sacks (or from 1 of each 10 barrels) and combine them to form 1 test sample. If sampled in bins or warehouses, take 1 test sample for each 200 barrels or fraction thereof.

(*c*) SAMPLING AT MILL.—Use any of the following methods that may be practicable, as ordered:

(1) *From the Conveyor Delivering to the Bin.*—Take at least 8 pounds of cement from approximately each 100 barrels passing over the conveyor.

(2) *From Filled Bins by Means of Proper Sampling Tubes.*—Tubes inserted vertically may be used for sampling cement to a maximum depth of 10 feet. Tubes inserted horizontally may be used where the construction of the bin permits. Samples shall be taken from points well distributed over the face of the bin.

(3) *From Filled Bins at Points of Discharge.*—Sufficient cement shall be taken from the discharge openings to obtain samples representative of the cement contained in the bin, as determined by the appearance at the discharge openings of indicators placed on the surface of the cement directly above these openings before drawing of the cement is started.

NOTE.—In sampling cement from sealed bins for a single customer, it is often customary to take one sample representing every 200 barrels and make all tests except tensile strength on each of these samples. Then make composite samples, using equal portions of 5 of the individual samples, and on these composite samples make 7- and 28-day tensile tests. (The tensile tests will thus cover 1 sample for every 1000 barrels.) As the cement is

shipped from the bin take 1 sample representing each carload and make setting and soundness tests only.

Preparation of Sample.—Pass the sample through a sieve having 20 meshes per linear inch in order to thoroughly mix the sample, break up lumps and remove foreign material.

Specific Gravity.—Determine the sp. gr. with the Le Chatelier apparatus, standardized by the Bureau of Standards. Use kerosene, free from water, or benzine not lighter than 62° Bé. Fill the flask with either of these liquids to a point on the stem between 0 and 1 cc. and introduce slowly 64 grams of cement of the same temperature as the liquid, taking care that the cement does not adhere to the inside of the flask above the liquid and to free the cement from air by rolling the flask in an inclined position. After all the cement is introduced, the level of the liquid will rise to some division of the graduated neck. The difference between readings is the volume displaced by 64 grams of the cement. Calculate the sp. gr. from the formula:

$$\text{Sp. gr.} = \frac{64}{\text{displaced volume (cc.)}}.$$

Keep the flask immersed in water during the operation to avoid variations in the temperature of the liquid in the flask (which should not exceed 0.5° C.) and report results to 2 decimal places. Check determinations should agree within 0.01.

Note.—The sp. gr. is to be determined on the cement as received; if it falls below 3.10 (or 3.07 for white cement), make a second determination after igniting the sample in a muffle at a temperature between 900 and 1000° C. Ignite at this temperature for 15 minutes and then for periods of 5 minutes to constant weight.

Fineness.—Place 50 grams of cement on a clean, dry 200-mesh sieve with pan and cover attached, if desired, and hold in one hand in a slightly inclined position so that the sample will be well distributed over the sieve, at the same time gently striking the side about 150 times per minute against the palm of the other hand on the upstroke. Turn the sieve every 25 strokes about $\frac{1}{6}$ of a revolution in the same direction. Continue the operation until not more than 0.05 gram passes through in 1 minute of continuous sieving. Weigh the residue on the sieve in grams and multiply by 2 to obtain the percentage of residue.

NOTES.—(1) Routine sieving is done in this laboratory on a Ro-tap mechanical sifter. The sifter is run for 15 minutes, the fine material in the pan discarded and then the sieving continued for 5-minute periods until no more material comes through the sieve. In case, however, any sample fails to pass on the Ro-tap tester, it shall not be rejected until checked by the hand method above described.

(2) The 200-mesh sieve used must be round, approximately 8 inches in diameter, and standardized by the U. S. Bureau of Standards. It should be made of woven (not twilled) wire cloth with 200 wires per inch and the number of wires in any whole inch should not be less than 192 nor more than 208. No opening between adjacent parallel wires should be more than 0.0050 inch. The diameter of the wire should be 0.0021 inch and the average diameter should not be less than 0.0019 nor more than 0.0023 inch. The value of the sieve as determined by sieving tests made in conformity with the standard specification for these tests on a standardized cement which gives a residue of 25–20% on the 200-mesh sieve, or on other similarly graded material, should not show a variation of more than 1.5% above or below the standards maintained at the Bureau of Standards.

(3) The old specifications required a 100-mesh sieve test. This test is made in the same way as the 200-mesh test, using a 100-mesh sieve of the following specifications:

Diameter of wire, inch	0.0042–0.0048
Meshes per linear inch	
Warp	95–101
Woof	93–103

Preparation of Neat Paste or Mortars.—The quantity of dry material to be mixed at one time must be between 500 and 1000 grams. Weigh out the dry materials to the nearest gram, place on a non-absorbent surface (glass is satisfactory), thoroughly mix dry, if sand is used, and form a crater in the center, into which pour the proper percentage of clean water. Turn the material on the outer edge into the crater by means of a trowel. After an interval of $\frac{1}{2}$ minute for the absorption of the water, complete the operation by continuous, vigorous mixing, squeezing and kneading with the hands for at least 1 minute. Protect the hands by rubber gloves during the mixing.

NOTES.—(1) The temperature of the room and the mixing water should be maintained as nearly as practicable at 21° C. (70° F.).

(2) In order to secure uniformity in the results of tests for the time of setting and tensile strength, the manner of mixing as above described should be carefully followed. At least 1 minute is necessary to obtain the desired plasticity, which is not appreciably affected by continuing the mixing for several minutes. The exact time necessary depends upon the personal equa-

tion of the operator. Any error in mixing should be on the side of over-mixing.

Normal Consistency.—Use the standard Vicat apparatus (Fig. 42), which consists of a frame bearing a movable rod weighing 300 grams, one end being 1 cm. in diameter for a distance of 6 cm. and the other having a removable needle 1 mm. in diameter, 6 cm. long. The rod is reversible and may be held in any desired position by a screw, and has midway between the ends a millimeter

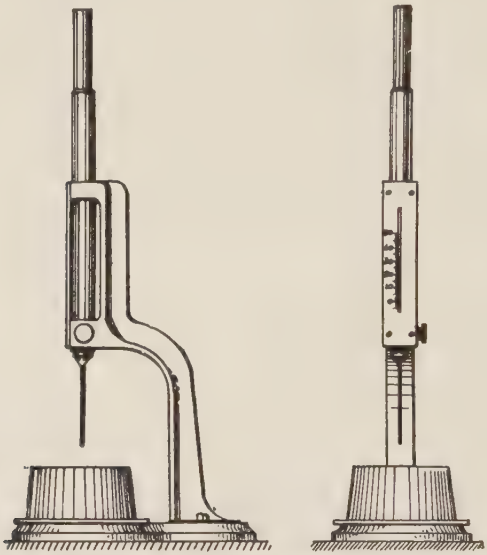


FIG. 42.—Vicat Apparatus.

scale attached to the frame. The paste is held in a conical, hard-rubber ring, 7 cm. in diameter at the base, 4 cm. high, resting on a glass plate about 10 cm. square.

In making the determination, weigh out 500 grams of cement and knead into a paste with a measured quantity of water as described previously. Quickly form into a ball with the hands, completing the operation by tossing it 6 times from one hand to the other, maintained about 6 inches apart.

Press the ball, resting in the palm of one hand, into the larger end of the rubber ring held in the other hand, completely filling

the ring with paste; then remove the excess at the larger end by a single movement of the palm of the hand. Place the ring on its larger end on the glass plate and slice off the excess paste at the smaller end (top) of the ring by a single oblique stroke of a trowel held at a slight angle with the top of the ring. During these operations take care not to compress the paste.

Place the paste confined in the ring, resting on the plate, under the rod and bring the larger end of the rod in contact with the surface of the paste; read the scale and quickly release the rod. The paste is considered to be of *normal consistency* when the rod settles to a point 10 mm. below the original surface in $\frac{1}{2}$ minute after being released.

The apparatus must be free from all vibrations during the test. Make trial pastes with varying percentages of water until the normal consistency is obtained. Express the amount of water required in percentage by weight of the dry cement.

Standard Mortar (1 : 3).—The consistency of standard mortar depends upon the amount of water required to produce a paste of normal consistency from the same sample of cement. Having determined the normal consistency of the cement sample, the consistency of standard mortar made from the same sample shall be as indicated in Table XXXVI below, the values being given in percentage of the dry weights of the cement and standard sand.

TABLE XXXVI—PERCENTAGE OF WATER FOR STANDARD MORTARS

Normal Consistency, Percentage of Water for Neat Cement Paste	Percentage of Water for 1 : 3 Mortar	Normal Consistency, Percentage of Water for Neat Cement Paste	Percentage of Water for 1 : 3 Mortar
15	9.0	23	10.3
16	9.2	24	10.5
17	9.3	25	10.7
18	9.5	26	10.8
19	9.7	27	11.0
20	9.8	28	11.2
21	10.0	29	11.3
22	10.2	30	11.5

Soundness.—Make a pat of cement paste of normal consistency about 3 inches in diameter, 0.5 inch thick at the center and tapering to a thin edge, on a clean glass plate about 4 inches square, and store it in moist air for 24 hours. In molding the pat, first flatten the cement paste on the glass and then form the pat by drawing the trowel from the outer edge toward the center.

Then place the pat in an atmosphere of steam at a temperature between 98 and 100° C. upon a suitable support 1 inch above boiling water for 5 hours. At the end of this time, examine the pat for shrinkage, absorption, cracking, checking or disintegration. The pat should be firm and sound.

NOTES.—(1) Unsoundness is usually manifested by change in volume which causes distortion, cracking, checking, or disintegration.

(2) Pats improperly made or exposed to drying may develop what are known as shrinkage cracks within the first 24 hours. These are not an indication of unsoundness.

(3) The failure of the pats to remain on the glass or the cracking of the glass to which the pats are attached does not necessarily indicate unsoundness.

(4) Should the pat leave the plate, distortion may be detected best with a straight edge applied to the surface which was in contact with the plate.

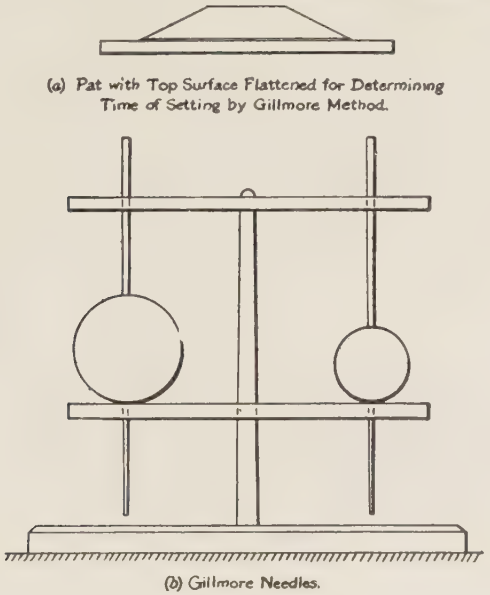
Time of Setting.—The time of setting may be determined either with the Vicat needle, previously described, or with the Gillmore needle. Unless otherwise directed, tests in this laboratory are made with the Gillmore needles.

(*a*) *With Gillmore Needles.*—Make a pat of neat cement about 3 inches in diameter and 0.5 inch in thickness with a flat top, mixed to normal consistency, and keep in moist air at a temperature maintained as nearly as practicable at 21° C. Test at intervals with the standard Gillmore needles (Fig. 43). The cement shall be considered as having acquired its *initial set* when the pat will bear, without appreciable indentation, the Gillmore needle $\frac{1}{12}$ inch in diameter, weighing 0.25 pound. The cement has acquired its *final set* when the pat will bear without an appreciable indentation, the Gillmore needle $\frac{1}{24}$ inch in diameter, weighing 1 pound. In making the test, hold the needles in a vertical position and apply lightly to the surface of the pat.

(*b*) *With Vicat Needle.*—Make a paste of neat cement of normal consistency and mold it into the hard-rubber ring, as previously described under Normal Consistency above. Place it under the

rod and then carefully bring the smaller end of the rod in contact with the surface of the paste and quickly release the rod. The paste has reached the condition of *initial set* when the needle ceases to pass a point 5 mm. above the glass plate in $\frac{1}{2}$ minute after being released; and *final set*, when the needle does not sink visibly into the paste.

The test pieces must be kept in moist air during the test.* The needle must be kept clean, as the collection of cement on the sides



(a) Pat with Top Surface Flattened for Determining Time of Setting by Gillmore Method.

(b) Gillmore Needles.

FIG. 43.

retards the penetration, and cement on the point may increase the penetration.

NOTE.—Time of setting is affected not only by the percentage and temperature of the water used and the amount of kneading the paste receives, but by the temperature and humidity of the air, and its determination is, therefore, only approximate.

Tensile Strength.—The tensile strength tests are made on briquettes having a cross-section of 1 square inch. For the neat

* This may be accomplished by placing them on a rack over water contained in a pan and covered by a damp cloth, kept from contact with them by a wire screen; or they may be stored in a moist closet.

tests use a neat paste made up to normal consistency. For mortar tests make a standard mortar according to Table XXXVI (p. 817), using 1 part of cement to 3 parts of standard Ottawa

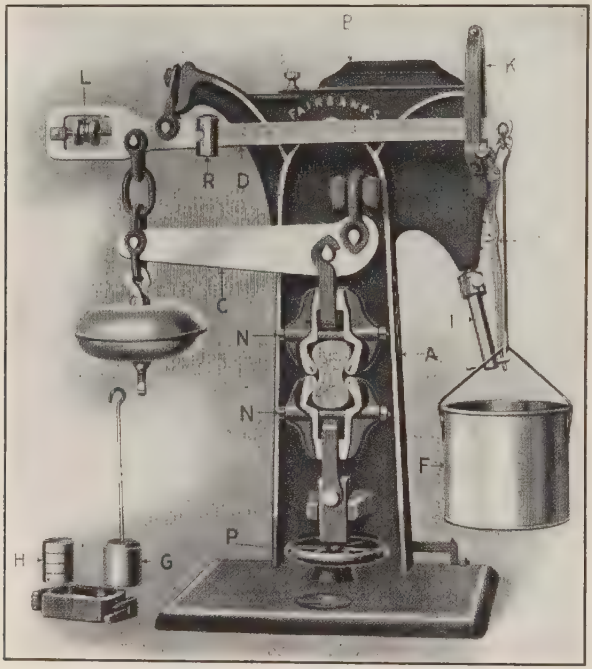


FIG. 44.—Fairbanks Cement Testing Machine.

DIRECTIONS FOR USE

Hang the cup *F* on the end of the beam *D*, as shown in the illustration. See that the poise *R* is at the zero mark, and balance the beam by turning the ball *L*. Fill the hopper *B* with the fine shot (of which a bag is provided with each machine). Place the briquette in the clamps *NN*. Tighten the hand wheel *P* sufficiently to cause the graduated beam *D* to rise to the stop *K*. Only enough pressure should be exerted to hold the beam firmly against the stop; not enough to transmit any strain to the specimen. Open the automatic valve *J* to allow the shot to run into the cup *F*. At the point where the spout joins the reservoir there is a small valve, by which the flow of shot may be regulated. Better results will be obtained by allowing the shot to run very slowly into the cup. When the briquette breaks, the beam *D* will drop and automatically close the valve *J*.

sand,* by weight. Use standard briquette molds as specified by the American Society for Testing Materials. Make 4 briquettes for each 28-day test and 3 for each of the other tests called for.

* See page 822.

Immediately after mixing, place the paste or mortar in the molds (wipe the molds with an oily cloth before using), pressing in firmly with the thumbs and smoothing off with a trowel without ramming. Then heap up additional mortar (or paste) above the mold and smooth off with a trowel. Draw the trowel over the mold in such a manner as to exert a moderate pressure on the material. Then turn the mold over and repeat the operation of heaping, thumbing, and smoothing off. Make the tests on the standard testing machine (Fig. 44), which should be frequently calibrated in order to determine its accuracy. The briquettes should be tested as soon as they are removed from the water. See that the bearing surfaces of the clips and briquettes are free from grains of sand or dirt. Carefully center the briquettes and apply the load continuously at the rate of 600 pounds per minute. In reporting results give the breaking strength of each briquette and the average of the 3 briquettes.

NOTES.—(1) The fourth briquette on the 28-day test is made up only for use in case anything goes wrong with one of the other briquettes. If any of the first 3 28-day briquettes appears to be faulty or gives a breaking strength widely at variance with the other 2, then use the fourth briquette in place of the faulty one. Otherwise do not break the fourth briquette.

(2) Briquettes which are manifestly faulty or which give strengths differing more than 15% from the average value of all test pieces made from the same samples and broken at the same period, shall not be considered in determining the tensile strength.

Storage of Test Briquettes.—The moist closet may consist of a soapstone, slate or concrete box, or a wooden box lined with metal. If a wooden box is used, the interior should be covered with felt or broad wicking kept wet. The bottom of the moist closet should be covered with water. The interior of the closet should be provided with non-absorbent shelves on which to place the test pieces.

Unless otherwise specified, all test pieces, immediately after molding, shall be placed in the moist closet for 20–24 hours. The briquettes should be kept in the molds on glass plates in the moist closet for at least 20 hours. After 20–24 hours in moist air the briquettes should be immersed in clean water in storage tanks of non-corroding material. The air and water should be maintained as nearly as possible at a temperature of 21° C. The briquettes for the various tests shall be stored as follows:

24-hour test: Twenty-four hours in moist air.

7-day test: One day (20–24 hrs.) in moist air, 6 days in water.

28-day test: One day in moist air, 27 days in water.

Standard Ottawa Sand.—Standard sand shall be natural sand from Ottawa, Illinois (obtained from the Ottawa Silica Company), and screened to pass a No. 20 sieve, but retained on a No. 30 sieve. The sand, having passed the No. 20 sieve, shall be considered standard when not more than 5 grams pass the No. 30 sieve after 1 minute of continuous sieving of a 500-gram sample.

Reference.—American Society for Testing Materials: "Triennial Standards," 633, ff. (1924).

CHEMICAL ANALYSIS OF PORTLAND CEMENT

General.—Portland cement, according to Le Chatelier, consists of a mixture of tri-calcium silicate and tri-calcium aluminate. It may also contain, and generally does contain, small amounts of magnesia and of calcium sulfate. The average analysis of 13 samples of different American Portland Cements* is as follows:

	Per cent
Silica, SiO_2	21.85
Iron oxide, Fe_2O_3	2.62
Alumina, Al_2O_3	7.03
Lime, CaO	62.50
Magnesia, MgO	2.06
Sulfur trioxide, SO_3	1.38
Loss on ignition	1.80

It is seldom necessary, however, to make a complete chemical analysis. A partial analysis will show whether the cement has been adulterated or is unsatisfactory.

Specifications.—The American Society for Testing Materials, under specifications C9-26, gives the following chemical requirements for Portland cement:

	Maximum Per cent
Loss on ignition	4.00
Insoluble residue	0.85
Sulfur trioxide, SO_3	2.00
Magnesia, MgO	5.00

* Meade: "Portland Cement," 16 (1906).

The methods given herewith, so far as they apply to the above determinations, are according to the American Society for Testing Materials requirements.

Loss on Ignition.—Heat 1 gram in a weighed, covered platinum crucible of 20–25-cc. capacity, using either of the following methods as ordered:

(A) Place the crucible in a hole in an asbestos board, clamped horizontally so that about $\frac{3}{5}$ of the crucible projects below, and blast at a full red heat for 15 minutes with an inclined flame. Cool in a desiccator and weigh. Check the loss in weight by a second blasting for 5 minutes. Take care to wipe off any particles of asbestos that may adhere to the crucible when withdrawn from the asbestos board.

(B) Place the crucible in a muffle heated to 900–1000° C. for 15 minutes, cool in a desiccator and weigh. Check the weight by a second heating for 5 minutes.

NOTE.—A permissible variation of 0.25% is allowed and all results between 4.00 and 4.25% shall be reported as 4.00%, when the cement is bought to American Society for Testing Materials specifications.

Insoluble Residue.—Treat 1 gram of the sample in a beaker with 10 cc. of water and 5 cc. of conc. HCl and warm until effervescence ceases. Dilute to 50 cc. and digest on the steam bath or hot plate until decomposition is complete. Filter the residue and wash with cold water. Digest the filter paper and contents in about 30 cc. of a 5% solution of Na_2CO_3, keeping the liquid at just below boiling for 15 minutes. Filter this residue, wash with cold water, then with a few drops of hot dil. HCl (1:9) and finally with hot water. Ignite at red heat, cool in a desiccator and weigh.

NOTE.—A permissible variation of 0.15% will be allowed and all results between 0.85 and 1.00% shall be reported as 0.85%, when the cement is purchased to American Society for Testing Materials specifications.

Sulfur Trioxide.—If the insoluble residue has been determined, use the acid filtrate for the determination of SO_3. Otherwise, dissolve 1 gram of the cement in 10 cc. of dil. HCl (1 : 1) with gentle warming. When solution is complete, add 40 cc. of water. Filter and wash the residue thoroughly with water. Dilute the filtrate to 250 cc., heat to boiling and add 10 cc. of a hot 10% solution of $BaCl_2$, slowly, drop by drop, from a pipette, and continue

boiling for 15 minutes. Digest on the steam bath until the precipitate has settled. Filter and wash with hot water. Place the paper and contents in a weighed platinum crucible and slowly char the paper until consumed without burning. Then ignite, cool in a desiccator and weigh as $BaSO_4$. Calculate to SO_3.

CALCULATION.—$BaSO_4 \times 0.3430 = SO_3$.

NOTE.—A permissible variation of 0.10% will be allowed and all results between 2.00 and 2.10% shall be reported as 2.00%, when the cement is purchased to American Society for Testing Materials specifications.

Silica.—Place 0.5 gram of the cement in an evaporating dish, add 10 cc. of water to prevent lumping and then 10 cc. of conc. HCl. Heat gently and agitate until decomposition is complete. Then evaporate to complete dryness on the steam bath. Heat the residue to about 150° C. for 0.5–1 hour. Take up with 20 cc. of dil. HCl (1 : 1), cover the dish and digest for 10 minutes on the steam bath. Dilute and filter through a quantitative filter, washing thoroughly with hot water. Evaporate the filtrate again to dryness on the steam bath. Take up with dil. HCl (1 : 1), digest for 10 minutes on the steam bath and filter through a fresh quantitative filter, washing with hot water. Place both papers in a weighed platinum crucible, dry, blast to constant weight and weigh as SiO_2.

NOTE.—If the silica determination is not required, it is not necessary to make the second evaporation, nor, of course, to weigh the SiO_2.

Iron Oxide and Alumina.—To the filtrate from the SiO_2 determination (about 250 cc.), add 5 cc. of conc. HCl and sufficient bromine water to precipitate any Mn which may be present. Make alkaline with NH_4OH, and boil until the odor of NH_3 is nearly but not quite gone. Let the precipitate settle and wash once by decantation and then slightly on the filter paper. Set aside the filtrate and transfer the precipitate by a jet of hot water to the original beaker. Dissolve in 10 cc. of hot conc. HCl and extract the filter paper with acid, adding the solution and washings to the main solution. Then reprecipitate at boiling heat by adding NH_4OH and bromine water in a volume of about 100 cc. Collect the precipitate, washing on the filter previously used, if this is still intact. Transfer to a weighed platinum crucible, ignite in a blast lamp, cool and weigh.

The above precipitate consists of $Fe_2O_3+Al_2O_3+Mn_3O_4$. For general purposes it is sufficient to report this as Iron Oxide and Alumina. If desired, the amounts of Fe_2O_3 and Mn_3O_4 may be determined and subtracted from the total precipitate to determine the amount of Al_2O_3. The amount of Mn is generally insignificant, and the iron may be determined by fusing the ignited precipitate with $KHSO_4$ and passing the solution of the fusion (made acid with H_2SO_4) through a Jones reductor, titrating the Fe with standard $KMnO_4$ solution (see p. 186).

Lime.—To the combined filtrates from the iron and alumina, somewhat evaporated if necessary, add 1 cc. of conc. NH_4OH, heat to boiling and add 25 cc. of a saturated, boiling solution of $(NH_4)_2C_2O_4$. Boil until the precipitate settles well, let stand for 1 hour, filter and wash with hot water. Place the filter while still wet in a platinum crucible (unweighed) and burn off the paper over a low flame, finally igniting until the paper is consumed. Dissolve this residue in HCl and dilute to 100 cc. Add NH_4OH in slight excess, heat to boiling and reprecipitate the lime with $(NH_4)_2C_2O_4$; let stand until settled clear; then filter and wash with hot water.

The precipitate of CaC_2O_4 may be dissolved in H_2SO_4 and titrated hot with 0.1 N $KMnO_4$ (see p. 697) or ignited strongly in a weighed platinum crucible, cooled in a desiccator and weighed rapidly as CaO.

Magnesia.—To the combined filtrates from the CaC_2O_4, add a slight excess of HCl, concentrate on the steam bath to about 150 cc., make slightly alkaline with NH_4OH, boil, and filter, if necessary. (There may be a slight precipitate of iron and alumina and perhaps calcium salts.) When cool, add 10 cc. of a saturated solution of $NaNH_4HPO_4$, with constant stirring. When the crystalline NH_4MgPO_4 has formed, add a moderate excess of conc. NH_4OH. Set aside for several hours, preferably overnight, filter and wash with water containing 2.5% of NH_3.* Dissolve the precipitate in a small quantity of hot HCl, dilute to about 100 cc. and add 1 cc. of a saturated solution of $NaNH_4HPO_4$ and then conc. NH_4OH, drop by drop with constant stirring, until the crystalline precipitate is again formed and the NH_4OH is in moderate excess. Let stand for about 2 hours. Filter through

* Conc. NH_4OH diluted 1 : 9.

an ignited and weighed Gooch crucible, washing as before. Ignite the precipitate to constant weight over a Meker burner or blast lamp not strong enough to soften or melt the pyrophosphate. Cool in a desiccator and weigh as $Mg_2P_2O_7$. Calculate to MgO.

CALCULATION.—$Mg_2P_2O_7 \times 0.3621 = MgO$.

NOTES.—(1) A permissible variation of 0.4% will be allowed and all results between 5.00 and 5.40% shall be reported as 5.00%, when the cement is bought to American Society for Testing Materials specifications.

(2) In case only the MgO is desired, all the steps in the above procedure must be followed, beginning under Silica with "Place 0.5 gram of the cement in an evaporating dish," etc., except that a double evaporation of the silica solution is not necessary, nor, of course, is it necessary to do anything with the iron and alumina precipitates or the second CaC_2O_4 precipitate.

REFERENCE.—American Society for Testing Materials: "Triennial Standards" 636–639 (1924).

MECHANICAL TESTING OF SAND AND GRAVEL FOR USE IN REINFORCED CONCRETE

General.—Sand and gravel for use in reinforced concrete construction have been the subject of considerable study, but thus far no official specifications for testing have appeared. The following methods, however, have been used for some time in this laboratory with good results. It is to be understood that they apply only to material for use with cement in concrete construction.

Definitions.—(1) SAND OR FINE AGGREGATE.—This consists of natural sand, crushed-stone or gravel screenings, graded from fine to coarse, and completely passing a $\frac{1}{4}$-inch screen in the dry condition. It should be free from dust, loam, soft particles, clay lumps, and organic matter. Not more than 6% should pass a 100-mesh sieve and it should be free from an excessive amount of mica.

(2) GRAVEL OR COARSE AGGREGATE.—This consists of natural gravel, crushed stone, cinders, or slag, graded from small to large particles, none of which, however, will pass through a $\frac{1}{4}$-inch screen. It should be clean and free from sticks, leaves, roots, or other organic matter. Bank gravel should be screened on a $\frac{1}{4}$-inch screen before mixing in construction work.

(3) SLAG.—When slag is used it should be clean, air-cooled blast-furnace slag weighing not less than 75 pounds per cubic foot and containing not over 1.3% of sulfur as sulfides.

(4) Cinders.—Where cinders are used as coarse aggregate they should be composed of hard, clean, vitreous clinker, free from unburned coal or ashes and from sulfides.

General Appearance.—Examine the sample as received and note whether or not it is clean and contains any of the impurities mentioned above.

Mechanical Analysis (Fineness).—The sample must be dry before starting screening tests.

Coarse or Mixed Aggregate.—If the sample apparently will practically all pass a $\frac{1}{4}$-inch sieve, weigh out 500 grams. If it contains many particles coarser than $\frac{1}{4}$ inch, weigh out a considerably larger amount, depending upon the proportion and size of the large particles. For samples containing particles as large as 2 inches, as much as 5–10 kilograms should be weighed.

Pass the sample successively through the various screens, beginning with the largest and continuing down to and including the $\frac{1}{4}$-inch screen. Weigh the residue retained on each screen. Calculate the amounts passing each screen as follows:

Subtract the amount remaining on the largest screen from the total amount of sample weighed out. This gives the weight passing this screen. From this weight subtract the amount remaining on the next screen. This gives the weight passing that screen. From the latter weight subtract the amount retained on the third screen; and so on. Calculate these weights to percentages of the original sample.

Mix well that portion of the sample which passed the $\frac{1}{4}$-inch screen and weigh out 200 grams. Make sieving tests on this as described below under Sand.

Notes.—(1) The screens generally used for coarse aggregate are $3\frac{1}{2}$, 3, $2\frac{1}{2}$, 2, $1\frac{1}{2}$, 1, $\frac{3}{4}$, $\frac{1}{2}$, and $\frac{1}{4}$ inch, respectively. They should have square openings of uniform size. The above figures refer to the size of the openings; the 1-inch screen, for example, has openings 1 inch square.

(2) The screening tests on the screens of $\frac{1}{4}$-inch and larger are calculated on the sample as received, whereas the figures on sieves smaller than $\frac{1}{4}$ inch should be calculated on the basis of the sand (material finer than $\frac{1}{4}$ inch).

(3) The $\frac{1}{4}$-inch sieve is taken as the dividing line between sand and gravel.

Sand.—If the sample is all finer than $\frac{1}{4}$ inch, weigh out 200 grams; otherwise weigh out 200 grams of the material which has passed a $\frac{1}{4}$-inch sieve. Place it on a 6-mesh sieve which is the topmost of a series of 7 brass sieves fitting into each other to

form a nest. The other sieves in the nest are 8, 10, 20, 30, 50, and 100 mesh, respectively. Put the cover on the top sieve and a receiver under the bottom one, and place the nest in a Ro-tap mechanical sieving machine. After 5 minutes' sieving, remove and weigh the residue in the bottom pan (passing 100 mesh). Return the pan and continue sieving for 5 minutes longer. Continue this until the increase in the amount of the fine residue in the pan is not more than 1 gram between subsequent shakings. Finally weigh the residue on each sieve and calculate the percentage *passing* each mesh as previously described.

The following example shows the method of tabulating the figures and the form of the final report. The figures to be reported are in the last column.

Screening Test of Sample as Received (5000 grams taken)

Screen	Grams Retained	Grams Passing	Per Cent Passing
3½ inch	None	5000	100.0
3 inch	500	4500	90.0
2½ inch	750	3750	75.0
2 inch	1000	2750	55.0
1½ inch	250	2500	50.0
1 inch	100	2400	48.0
¾ inch	275	2125	42.5
½ inch	500	1625	32.5
¼ inch	500	1125	22.5

Sieving Test of Sand Passing ¼-inch Screen (200 grams taken)

Sieve	Grams Retained	Grams Passing	Per Cent Passing
¼ inch	None	200	100.0
6 mesh	24	176	88.0
8 mesh	33	143	71.5
10 mesh	27	116	58.0
20 mesh	35	81	40.5
30 mesh	30	51	25.5
50 mesh	21	30	15.0
100 mesh	21	9	4.5

NOTES.—(1) Some contractors require also a 200-mesh sieve test. In this case use the cement sieve described on page 815.

(2) Sieving may be done by hand, using the sieves consecutively, always starting with the largest; but much time is saved by the Ro-tap and it eliminates the personal factor of the operator.

(3) The sieves used should be accurately made and should be carefully tested out unless certified by the U. S. Bureau of Standards. The American Society for Testing Materials specifications for standard sieves* are as follows:

Mesh Designation	Actual Mesh (per inch)	Opening (inch)	Wire Diameter (inch)	Permissible Variations above and below Standard	
				Mesh (per inch)	Diameter (inch)
10	9.9	0.079	0.022	0.1	0.002
20	20.3	0.0335	0.0157	0.5	0.0006
30	30.5	0.0197	0.0130	1.0	0.0005
40	40.6	0.0142	0.0102	1.5	0.0004
50	50.8	0.0114	0.0083	2.0	0.0004
80	78.7	0.0067	0.0059	3.0	0.0003
100	99.1	0.0055	0.0046	3.0	0.0003
200	200.7	0.0029	0.0021	8.0	0.0002

Tensile Strength.—Make up seven 1:3 mortar briquettes with standard Ottawa sand and any of the standard brands of Portland cement,† as described on page 819 under Tensile Strength.

Make up 7 more briquettes using *the same cement*, but, instead of standard Ottawa sand, use the sand in question (after removing any material coarser than $\frac{1}{4}$ inch). Both sets of briquettes should be made up to standard mortar, based on the normal consistency of the cement used, and the percentage of water used should be stated. In the case of bank sand or crushed stone containing considerable fine material, it will be found that

* "Triennial Standards" 939 (1924).

† The cement should be tested according to American Society for Testing Materials specifications (see p. 811), and not used if it does not meet these specifications.

more water is required to make a mortar of the proper consistency than in the case of the standard Ottawa sand.

Break 3 briquettes of each set at the end of 7 days and 3 at the end of 28 days, respectively. The fourth briquette of the 28-day sets is only to be broken in case anything goes wrong with one of the other three (see p. 821, under Note 1). Divide the average strength of the sample briquettes by the average strength of the standard sand briquettes broken at the same time, and multiply by 100 to obtain the percentage strength of the sample as compared with the standard.

The following example shows the method of reporting:

Tensile Strength, Pounds per Square Inch:

	1 cement: 3 sand
7 days	248–270–264
Average	261
28 days	380–340–355
Average	358
Percentage of water used	11.0%

	1 cement: 3 *standard* sand
7 days	238–258–250
Average	259
28 days	370–328–341
Average	346
Percentage of water used	10.2%

Percentage Strength of Standard Sand:

7 days	105%
28 days	103%

NOTES.—(1) A well-graded, clean sand should show a tensile strength more than 100% that of the standard sand at both periods. It is usually recommended that a sand which shows less than 70% of the standard sand's strength at the end of 28 days should be rejected for use in reinforced concrete work. A satisfactory sand should also show a greater actual strength at the end of 28 days than at the end of 7 days.

(2) Any obviously defective briquette should not be counted in the average, nor any result which varies more than 50 pounds from the average.

Clay and Silt.*—Moisten the sample as received, mix thoroughly and dry to constant weight at 100–110° C. Dry and accurately weigh a pan or vessel about 12 inches in diameter

* American Society for Testing Materials, Standard D72-21.

and not less than 4 inches deep. Into this pan weigh a representative portion of the dry sample, weighing not less than fifty times the weight of the largest stone in the sample. Pour sufficient water into the pan to cover the sample and agitate vigorously for 15 seconds with a stirring rod or a trowel. Let settle for 15 seconds and pour off the water into a weighed evaporating dish, taking care not to pour off any sand or gravel. Repeat this operation until the wash water is clear; then dry the washed material to constant weight at 100–110° C. Calculate the percentage of clay and silt from the loss in weight due to the washing.

As a check on the result thus obtained, evaporate the wash water to dryness, weigh the residue, and calculate its percentage.

Color Test for Organic Matter.—The method is based on a comparison of the color produced by the reaction of NaOH upon the organic matter in the sand with standard colors produced from known amounts of alkaline sodium tannate.

To 200 grams of the dry sample (passing $\frac{1}{4}$ inch), add 100 cc. of 3% NaOH solution and digest at room temperature with occasional stirring for 24 hours. Filter and refilter, if necessary, until the filtrate is absolutely clear. Place 10 cc. of the final clear filtrate in a 50-cc. Nessler tube and dilute to 50 cc. with distilled water. Mix thoroughly and let stand until all foam and bubbles disappear. Determine the Color Value of the liquid by comparing it with tubes containing standard solutions of alkaline sodium tannate, looking through the full depth of the solution with the cylinders held toward a good natural light.

Standard Tannate Solution.—The preparation of the standard solution for comparing the colors should be begun at the same time as the treatment of the sand. Add 10 cc. of a 2% solution of tannic acid in 10% alcohol to 90 cc. of a 3% solution of NaOH and let stand 24 hours at room temperature. Place 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 cc., respectively, of this solution in 50-cc. Nessler tubes, dilute to the mark with distilled water and mix.

The following table shows the amount of tannic acid in each cylinder and the color value of the solution expressed in parts of tannic acid per million parts by weight:

Tannate Solution, *cc.*	Tannic Acid, *mgs.*	Color Value
1	2	100
2	4	200
3	6	300
4	8	400
5	10	500
6	12	600
7	14	700
8	16	800
9	18	900
10	20	1000

It is desirable to have good sunlight for comparing the colors. If sunlight is not available, the amount of tannic acid in each of the standard tubes may be decreased by $\frac{1}{2}$ and the other values of the table modified accordingly.

In case the solution obtained by digesting the sand with the NaOH is very dark, use less than 10 cc. for the comparison, and make the necessary modifications in the calculation. With very light-colored solutions, use more than 10 cc. of the filtrate. The depth of the color of the solution decreases on standing, hence the solution should be made up fresh for each day's work.

Calculation.—Using 10 cc. of the filtrate from the 200-gram sample, the color value of the sand is the same as that of the standard tube which it most nearly matches. If 5 cc. of the filtrate are used, the color values should be doubled. Similar corrections should be made if any other volume than 10 cc. is employed.

Notes.—(1) This color test was developed by Abrams and Harder, published in *Circ.* No. 1, Structural Materials Research Laboratory, Lewis Institute, Chicago (1917).

(2) Sand showing a color value greater than 250 should be looked upon with suspicion for use in reinforced concrete. Most good sands give color values between 0 and 100.

(3) For a simple field test based upon the above method see American Society for Testing Materials: "Triennial Standards," 766 (1924).

ANALYTICAL TABLES

In the following tables the weights and calculations are based on the table of International Atomic Weights for 1925. In computing the molecular weights in Table AII the number of decimal places has been governed by the least number of decimal places in any one of the atomic weights of the elements entering into the chemical formula. For example, in the case of H_2MoO_4 the calculated molecular weight would be $2\times1.008+96.0+4\times16.000=162.016$. Since, however, the atomic weight of Mo is given only to one decimal place, the molecular weight of the compound should also contain only one decimal place and therefore will be found in Table AII as 162.0. In the tables of equivalents of volumetric solutions the values have, in most cases, been carried out to a sufficient number of places to give an accuracy of at least 0.1%; and for purposes of uniformity the factors in Table AIII have, as a rule, been calculated to four decimal places. In a few cases, where the values are more or less approximate or empirical, they are carried to a lesser number of decimal places.

Five-place logarithms have been used throughout the tables for uniformity and greater accuracy. In most cases, however, sufficient accuracy would be obtained from four-place logarithms and the analyst is advised to "round off" the last place of the logarithms given, unless unusual accuracy is required.

TABLE AI

INTERNATIONAL ATOMIC WEIGHTS, 1925

Element	Symbol	Atomic Weight	Logarithm
Aluminum	Al	26.97	1.43088
Antimony	Sb	121.77	2.08554
Argon	A	39.91	1.60108
Arsenic	As	74.96	1.87483
Barium	Ba	137.37	2.13789
Beryllium	Be	9.02	0.95521
Bismuth	Bi	209.00	2.32015
Boron	B	10.82	1.03423
Bromine	Br	79.916	1.90264
Cadmium	Cd	112.41	2.05081
Calcium	Ca	40.07	1.60282
Carbon	C	12.000	1.07918
Cerium	Ce	140.25	2.14691
Cesium	Cs	132.81	2.12323
Chlorine	Cl	35.457	1.54970
Chromium	Cr	52.01	1.71609
Cobalt	Co	58.94	1.77041
Columbium	Cb	93.1	1.96895
Copper	Cu	63.57	1.80325
Dysprosium	Dy	162.52	2.21090
Erbium	Er	167.7	2.22453
Europium	Eu	152.0	2.18184
Fluorine	F	19.00	1.27875
Gadolinium	Gd	157.26	2.19662
Gallium	Ga	69.72	1.84336
Germanium	Ge	72.60	1.86094
Glucinum	Gl	(See Beryllium)	
Gold	Au	197.2	2.29491
Helium	He	4.00	0.60206
Holmium	Ho	163.4	2.21325
Hydrogen	H	1.008	0.00346
Indium	In	114.8	2.05994
Iodine	I	126.932	2.10357
Iridium	Ir	193.1	2.28578
Iron	Fe	55.84	1.74695
Krypton	Kr	82.9	1.91855
Lanthanum	La	138.90	2.14270
Lead	Pb	207.20	2.31639
Lithium	Li	6.940	0.84136

TABLE AI—International Atomic Weights, 1925—(*Continued*)

Element	Symbol	Atomic Weight	Logarithm
Lutecium	Lu	175.0	2.24304
Magnesium	Mg	24.32	1.38596
Manganese	Mn	54.93	1.73981
Mercury	Hg	200.61	2.30235
Molybdenum	Mo	96.0	1.98227
Neodymium	Nd	144.27	2.15918
Neon	Ne	20.2	1.30535
Nickel	Ni	58.69	1.76856
Niobium	Nb	(See Columbium)	
Niton	Nt	(See Radon)	
Nitrogen	N	14.008	1.14638
Osmium	Os	190.8	2.28058
Oxygen	O	16.000	1.20412
Palladium	Pd	106.7	2.02816
Phosphorus	P	31.027	1.49174
Platinum	Pt	195.23	2.29055
Potassium	K	39.096	1.59214
Praseodymium	Pr	140.92	2.14897
Radium	Ra	225.95	2.35402
Radon	Rn	222.	2.34635
Rhodium	Rh	102.91	2.01246
Rubidium	Rb	85.44	1.93166
Ruthenium	Ru	101.7	2.00732
Samarium	Sm	150.43	2.17734
Scandium	Sc	45.10	1.65418
Selenium	Se	79.2	1.89873
Silicon	Si	28.06	1.44809
Silver	Ag	107.880	2.03294
Sodium	Na	22.997	1.36167
Strontium	Sr	87.63	1.94265
Sulfur	S	32.064	1.50602
Tantalum	Ta	181.5	2.25888
Tellurium	Te	127.5	2.10551
Terbium	Tb	159.2	2.20194
Thallium	Tl	204.39	2.31046
Thorium	Th	232.15	2.36577
Thulium	Tm	169.4	2.22891
Tin	Sn	118.70	2.07445
Titanium	Ti	48.1	1.68215

TABLE AI—International Atomic Weights, 1925—(*Concluded*)

Element	Symbol	Atomic Weight	Logarithm
Tungsten	W	184.0	2.26482
Uranium	U	238.17	2.37689
Vanadium	V	50.96	1.70723
Xenon	Xe	130.2	2.11461
Ytterbium	Yb	173.6	2.23955
Yttrium	Y	88.9	1.94890
Zinc	Zn	65.38	1.81544
Zirconium	Zr	91.	1.95904

TABLE AII

Molecular and Atomic-Group Weights

Name	Formula	Molecular Weight	Logarithm
Acetaldehyde	CH_3CHO	44.032	1.64377
(Acetate Radical)	$C_2H_3O_2$	59.024	1.77103
Acetic Anhydride	$(CH_3CO)_2O$	102.048	2.00881
Acetone	$(CH_3)_2CO$	58.048	1.76379
(Acetyl Radical)	C_2H_3O	43.024	1.63371
Acetylene	C_2H_2	26.016	1.41524
Acid, Abietic	$HC_{20}H_{29}O_2$	302.240	2.48035
Acetic	$HC_2H_3O_2$	60.032	1.77838
Arachidic	$HC_{20}H_{39}O_2$	312.320	2.49460
Arsenic	$H_3AsO_4 \cdot \frac{1}{2}H_2O$	150.99	2.17895
Arsenic, Anhydrous	H_3AsO_4	141.98	2.15223
Benzoic	$HC_7H_5O_2$	122.048	2.08654
Bichromic	$H_2Cr_2O_7$	218.04	2.33854
Boric	H_3BO_3	61.84	1.79127
Butyric	$HC_4H_7O_2$	88.064	1.94480
Carbonic	H_2CO_3	62.016	1.79250
Chlorauric, Anhydrous	$HAuCl_4$	340.0	2.53148
Chlorauric, Crystalline	$HAuCl_4 \cdot 4H_2O$	412.1	2.61500
Chloric, Anhydrous	$HClO_3$	84.465	1.92668
Chloric, Crystalline	$HClO_3 \cdot 7H_2O$	210.577	2.32342
Chlorplatinic, Anhydrous	H_2PtCl_6	409.99	2.61277
Chlorplatinic, Crystalline	$H_2PtCl_6 \cdot 6H_2O$	518.08	2.71439
Chlorplatinous	H_2PtCl_4	339.07	2.53029
Chromic	H_2CrO_4	118.03	2.07199
Citric, Anhydrous	$H_3C_6H_5O_7$	192.064	2.28345
Citric, Crystalline	$H_3C_6H_5O_7 \cdot H_2O$	210.080	2.32239
Fluosilicic	H_2SiF_6	144.08	2.15860
Formic	$HCHO_2$	46.016	1.66291
Hydriodic	HI	127.940	2.10701
Hydrobromic	HBr	80.924	1.90808
Hydrochloric	HCl	36.465	1.56188
Hydrocyanic	HCN	27.016	1.43162
Hydrofluoric	HF	20.01	1.30125
Iodic	HIO_3	175.940	2.24537
Lactic	$HC_3H_5O_3$	90.048	1.95447
Malic	$H_2C_4H_4O_5$	134.048	2.12726
Molybdic, Anhydrous	H_2MoO_4	162.0	2.20952
Molybdic, Hydrated	$H_2MoO_4 \cdot H_2O$	180.0	2.25527
Nitric	HNO_3	63.016	1.79945

TABLE AII—Molecular and Atomic-Group Weights—(*Continued*)

Name	Formula	Molecular Weight	Logarithm
Acid, Nitrosylsulfuric	$HNOSO_4$	127.080	2.10408
Nitrous	HNO_2	47.016	1.67224
Oleic	$HC_{18}H_{33}O_2$	282.272	2.45067
Oxalic, Anhydrous	$H_2C_2O_4$	90.016	1.95432
Oxalic, Crystalline	$H_2C_2O_4 \cdot 2H_2O$	126.048	2.10054
Palmitic	$HC_{16}H_{31}O_2$	256.256	2.40868
Perchloric, Anhydrous	$HClO_4$	100.465	2.00201
Perchloric, Crystalline	$HClO_4 \cdot 2H_2O$	136.497	2.13512
Persulfuric	$H_2S_2O_8$	194.144	2.28813
Phosphoric, Hypo-	H_2PO_3	81.043	1.90872
Phosphoric, Meta-	HPO_3	80.035	1.90328
Phosphoric, Ortho-	H_3PO_4	98.051	1.99145
Phosphoric, Pyro-	$H_4P_2O_7$	178.086	2.25063
Phosphorous, Hypo-	H_3PO_2	66.051	1.81988
Phosphorous, Ortho-	H_3PO_3	82.051	1.91409
Phosphotungstic	$P_2O_5 \cdot 12WO_3 \cdot 42H_2O$	3682.7	3.56616
Prussic (See Acid, Hydrocyanic)			
Pyrosulfuric	$H_2S_2O_7$	178.144	2.25077
Salicylic	$HC_7H_5O_3$	138.048	2.14003
Selenic, Anhydrous	H_2SeO_4	145.2	2.16197
Selenic, Crystalline	$H_2SeO_4 \cdot H_2O$	163.2	2.21272
Selenious	H_2SeO_3	129.2	2.11126
Silicic, Meta-	H_2SiO_3	78.08	1.89254
Silicic, Ortho-	H_2SiO_4	94.08	1.97350
Silicotungstic	$4H_2SiO_3 \cdot 12WO_3 \cdot 22H_2O$	3492.7	3.54316
Stearic	$HC_{18}H_{35}O_2$	284.288	2.45376
Sulfocyanic	$HCNS$	59.080	1.77144
Sulfuric	H_2SO_4	98.080	1.99158
Sulfurous	H_2SO_3	82.080	1.91424
Tannic	$C_{14}H_{10}O_9$	322.080	2.50796
Tartaric, Anhydrous	$H_2C_4H_4O_6$	150.048	2.17623
Tartaric, Crystalline	$H_2C_4H_4O_6 \cdot H_2O$	168.064	2.22548
Tungstic	H_2WO_4	250.0	2.39794
Alum	$K_2Al_2(SO_4)_4 \cdot 24H_2O$	948.77	2.97716
Alumina (See Aluminum Oxide)			
Aluminum Acetate	$Al(C_2H_3O_2)_3$	204.04	2.30971
Chloride, Anhydrous	$AlCl_3$	133.34	2.12496

TABLE AII—Molecular and Atomic-Group Weights—(*Continued*)

Name	Formula	Molecular Weight	Logarithm
Aluminum Chloride, Crystalline	$AlCl_3 \cdot 6H_2O$	241.44	2.38281
Fluoride, Anhydrous	AlF_3	83.97	1.92412
Fluoride, Crystalline	$AlF_3 \cdot 3\frac{1}{2}H_2O$	147.03	2.16741
Hydroxide	$Al(OH)_3$	77.99	1.89204
Oleate	$Al(C_{18}H_{33}O_2)_3$	870.76	2.93990
Oxide	Al_2O_3	101.94	2.00834
Phosphate	$AlPO_4$	122.00	2.08636
Potassium Fluoride (See Potassium Aluminum Fluoride)			
Potassium Silicate (See Potassium Aluminum Silicate)			
Potassium Sulfate (See Alum)			
Silicate	$Al_2Si_2O_7 \cdot H_2O$	240.08	2.38035
Sulfate, Anhydrous	$Al_2(SO_4)_3$	342.13	2.53419
Sulfate, Crystalline	$Al_2(SO_4)_3 \cdot 18H_2O$	666.42	2.82374
(Amino Radical)	NH_2	16.024	1.20477
Ammonia	NH_3	17.032	1.23126
(Ammonium Radical)	NH_4	18.040	1.25624
Ammonium Acetate	$NH_4C_2H_3O_2$	77.064	1.88685
Alum	$(NH_4)_2Al_2(SO_4)_4 \cdot 24H_2O$	906.64	2.95745
Bichromate	$(NH_4)_2Cr_2O_7$	252.10	2.40157
Bromide	NH_4Br	97.956	1.99103
Carbonate	$(NH_4)_2CO_3 \cdot NH_4CO_2 \cdot NH_2$	174.144	2.24091
Carbonate, Crystalline	$(NH_4)_2CO_3 \cdot H_2O$	114.096	2.05727
Chloride	NH_4Cl	53.497	1.72833
Chlorplatinate	$(NH_4)_2PtCl_6$	444.05	2.64743
Chromate	$(NH_4)_2CrO_4$	152.09	2.18210
Chrome Alum	$(NH_4)_2Cr_2(SO_4)_4 \cdot 24H_2O$	956.74	2.98080
Citrate	$(NH_4)_3C_6H_5O_7$	243.160	2.38589
Copper Chloride (See Cupric Ammonium Chloride)			
Ferric Alum (See Ferric Ammonium Alum)			
Ferrous Sulfate (See Ferrous Ammonium Sulfate)			
Fluoride	NH_4F	37.04	1.56867
Hydroxide	NH_4OH	35.048	1.54466
Iodide	NH_4I	144.972	2.16129
Iron Alum (See Ferric Ammonium Alum)			
Magnesium Chloride, etc. (See Magnesium Ammonium Chloride, etc.)			
Molybdate	$(NH_4)_2MoO_4$	196.1	2.29248

TABLE AII—Molecular and Atomic-Group Weights—(*Continued*)

Name	Formula	Molecular Weight	Logarithm
Ammonium Nickel Chloride (See Nickel Ammonium Chloride)			
Nitrate	NH_4NO_3	80.048	1.90335
Oleate	$NH_4C_{18}H_{33}O_2$	299.304	2.47612
Oxalate, Anhydrous	$(NH_4)_2C_2O_4$	124.080	2.09370
Oxalate, Crystalline	$(NH_4)_2C_2O_4 \cdot H_2O$	142.096	2.15258
(Oxide Radical)	$(NH_4)_2O$	52.080	1.71667
Persulfate	$(NH_4)_2S_2O_8$	228.208	2.35833
Phosphate, Di-	$(NH_4)_2HPO_4$	132.115	2.12095
Phosphate, Mono-	$NH_4H_2PO_4$	115.083	2.06101
Phosphomolybdate, Di-	$(NH_4)_2HPO_4 \cdot 12MoO_3$	1860.1	3.26953
Phosphomolybdate, Tri-	$(NH_4)_3PO_4 \cdot 12MoO_3$	1877.1	3.27348
Sodium Hydrogen Phosphate, Anhydrous	NH_4NaHPO_4	137.072	2.13695
Sodium Hydrogen Phosphate, Crystalline	$NH_4NaHPO_4 \cdot 4H_2O$	209.136	2.32043
Sulfate	$(NH_4)_2SO_4$	132.144	2.12105
Sulfhydrate	NH_4SH	51.112	1.70853
Sulfide	$(NH_4)_2S$	68.144	1.83343
Sulfocyanate	NH_4CNS	76.112	1.88145
Zinc Phosphate (See Zinc Ammonium Phosphate)			
Amyl Acetate	$C_5H_{11}C_2H_3O_2$	130.112	2.11432
Alcohol	$C_5H_{11}OH$	88.096	1.94496
Aniline	$C_6H_5NH_2$	93.064	1.96878
Antimonic Oxychloride	$SbOCl_3$	244.14	2.38764
Antimonous Oxychloride	$SbOCl$	173.23	2.23863
Antimony Pentachloride	$SbCl_5$	299.06	2.47576
Pentasulfide	Sb_2S_5	403.86	2.60623
Pentoxide	Sb_2O_5	323.54	2.50993
Tetroxide	Sb_2O_4	307.54	2.48791
Trichloride	$SbCl_3$	228.14	2.35821
Trioxide	Sb_2O_3	291.54	2.46470
Trisulfide	Sb_2S_3	339.73	2.53114
Antimonyl Potassium Tartrate (See Potassium Antimonyl Tartrate)			
Arabinose	$C_5H_{10}O_5$	150.080	2.17632
(Arsenate Radical)	AsO_4	138.96	2.14289
(Arsenate Radical, Pyro-)	As_2O_7	261.92	2.41817
Arsenic Disulfide	As_2S_2	214.05	2.33052

TABLE AII—Molecular and Atomic-Group Weights—(*Continued*)

Name	Formula	Molecular Weight	Logarithm
Arsenic Pentasulfide	As_2S_5	310.24	2.49170
Pentoxide	As_2O_5	229.92	2.36158
(Arsenite Radical)	AsO_3	122.96	2.08977
Arsenous Chloride	$AsCl_3$	181.33	2.25847
Hydride	AsH_3	77.98	1.89198
Oxide	As_2O_3	197.92	2.29649
Sulfide	As_2S_3	246.11	2.39113
Arsine (See Arsenous Hydride)			
Auric Chloride Anhydrous	$AuCl_3$	303.6	2.48230
Chloride, Crystalline	$AuCl_3{\cdot}2H_2O$	339.6	2.53097
Barium Carbonate	$BaCO_3$	197.37	2.29528
Chloride, Anhydrous	$BaCl_2$	208.28	2.31865
Chloride, Crystalline	$BaCl_2{\cdot}2H_2O$	244.32	2.38796
Chromate	$BaCrO_4$	253.38	2.40378
Fluosilicate	$BaSiF_6$	279.43	2.44628
Hydroxide, Anhydrous	$Ba(OH)_2$	171.39	2.23399
Hydroxide, Crystalline	$Ba(OH)_2{\cdot}8H_2O$	315.51	2.49901
Nitrate	$Ba(NO_3)_2$	261.39	2.41729
Oxide	BaO	153.37	2.18574
Peroxide, Anhydrous	BaO_2	169.37	2.22884
Peroxide, Crystalline	$BaO_2{\cdot}8H_2O$	313.50	2.49624
Phosphate, Tri-	$Ba_3(PO_4)_2$	602.16	2.77971
Sulfate	$BaSO_4$	233.43	2.36816
Sulfide	BaS	169.43	2.22899
Benzaldehyde	C_6H_5CHO	106.048	2.02551
Benzene	C_6H_6	78.048	1.89236
(Benzyl Radical)	C_6H_5	77.040	1.88672
(Bicarbonate Radical)	HCO_3	61.008	1.78539
(Bichromate Radical)	Cr_2O_7	216.02	2.33449
Bismuth Nitrate, Anhydrous	$Bi(NO_3)_3$	395.02	2.59662
Nitrate, Crystalline	$Bi(NO_3)_3{\cdot}5H_2O$	485.10	2.68583
Oxychloride	$BiOCl$	260.46	2.41574
Phosphate	$BiPO_4$	304.03	2.48292
Subnitrate	$BiONO_3{\cdot}H_2O$	305.02	2.48433
Sulfide	Bi_2S_3	514.19	2.71112
Trioxide	Bi_2O_3	466.00	2.66839
Bleaching Powder (See Calcium Oxychloride)			
Bone Phosphate (See Calcium Phosphate, Tri-)			
(Borate Radical, Tetra-)	B_4O_7	155.28	2.19111

TABLE AII—Molecular and Atomic-Group Weights—(*Continued*)

Name	Formula	Molecular Weight	Logarithm
Borax (See Sodium Tetraborate, Crystalline)			
Boric Oxide	B_2O_3	69.64	1.84286
Borneol	$C_{10}H_{17}OH$	154.144	2.18792
Bornyl Acetate	$C_{10}H_{17}C_2H_3O_2$	196.160	2.29261
Butyric Anhydride	$(C_3H_7CO)_2O$	158.112	2.19896
Cadmium Chloride, Anhydrous	$CdCl_2$	183.32	2.26321
Chloride, Crystalline	$CdCl_2 \cdot 2H_2O$	219.36	2.34116
Hydroxide	$Cd(OH)_2$	146.43	2.16563
Iodide	CdI_2	366.27	2.56380
Nitrate, Anhydrous	$Cd(NO_3)_2$	236.43	2.37370
Nitrate, Crystalline	$Cd(NO_3)_2 \cdot 4H_2O$	308.49	2.48925
Oxide	CdO	128.41	2.10860
Sulfate, Anhydrous	$CdSO_4$	208.47	2.31905
Sulfate, Crystalline	$CdSO_4 \cdot \frac{8}{3}H_2O$	256.52	2.40912
Sulfate, Crystalline	$CdSO_4 \cdot 4H_2O$	280.54	2.44799
Sulfide	CdS	144.47	2.15978
Caffeine	$C_8H_{10}N_4O_2$	194.112	2.28806
Calcium Acetate, Anhydrous	$Ca(C_2H_3O_2)_2$	158.12	2.19899
Acetate, Crystalline	$Ca(C_2H_3O_2)_2 \cdot H_2O$	176.13	2.24584
Arsenate	$Ca_3(AsO_4)_2$	398.13	2.60002
Bicarbonate	$CaH_2(CO_3)_2$	162.09	2.20975
Bisulfite (Meta)	CaS_2O_5	184.20	2.26529
Carbide	CaC_2	64.07	1.80665
Carbonate	$CaCO_3$	100.07	2.00030
Chloride, Anhydrous	$CaCl_2$	110.98	2.04524
Chloride, Crystalline (Hexahydrate)	$CaCl_2 \cdot 6H_2O$	219.08	2.34060
Chloride, Crystalline (Monohydrate)	$CaCl_2 \cdot H_2O$	129.00	2.11059
Fluoride	CaF_2	78.07	1.89248
Hydroxide	$Ca(OH)_2$	74.09	1.86976
Hypochlorite, Anhydrous	$Ca(ClO)_2$	142.98	2.15528
Hypochlorite, Hydrous	$Ca(ClO)_2 \cdot 4H_2O$	215.05	2.33254
Nitrate, Anhydrous	$Ca(NO_3)_2$	164.09	2.21508
Nitrate, Crystalline	$Ca(NO_3)_2 \cdot 4H_2O$	236.15	2.37319
Oleate	$Ca(C_{18}H_{33}O_2)_2$	602.60	2.78003
Oxalate, Anhydrous	CaC_2O_4	128.07	2.10745
Oxalate, Crystalline	$CaC_2O_4 \cdot H_2O$	146.09	2.16462
Oxide	CaO	56.07	1.74873

TABLE AII—Molecular and Atomic-Group Weights—(*Continued*)

Name	Formula	Molecular Weight	Logarithm
Calcium Oxychloride	$CaOCl_2$	126.98	2.10373
Peroxide	CaO_2	72.07	1.85775
Phosphate, Di-, Anhydrous	$CaHPO_4$	136.11	2.13389
Phosphate, Di-, Crystalline	$CaHPO_4{\cdot}2H_2O$	172.14	2.23588
Phosphate, Mono-, Anhydrous	$CaH_4(PO_4)_2$	234.16	2.36951
Phosphate, Mono-, Crystalline	$CaH_4(PO_4)_2{\cdot}H_2O$	252.17	2.40170
Phosphate, Tri-	$Ca_3(PO_4)_2$	310.26	2.49172
Silicate	$CaSiO_3$	116.13	2.06494
Stearate	$Ca(C_{18}H_{35}O_2)_2$	606.63	2.78292
Sulfate, Anhydrous	$CaSO_4$	136.13	2.13396
Sulfate, Crystalline	$CaSO_4{\cdot}2H_2O$	172.17	2.23596
Sulfide	CaS	72.13	1.85812
Sulfite, Anhydrous	$CaSO_3$	120.13	2.07965
Sulfite, Crystalline	$CaSO_3{\cdot}2H_2O$	156.17	2.19360
Thiosulfate, Anhydrous	CaS_2O_3	152.20	2.18241
Thiosulfate, Crystalline	$CaS_2O_3{\cdot}6H_2O$	260.30	2.41547
Carbon Bisulfide	CS_2	76.128	1.88155
Dioxide	CO_2	44.000	1.64345
Monoxide	CO	28.000	1.44716
Tetrachloride	CCl_4	153.828	2.18704
(Carbonate Radical)	CO_3	60.000	1.77815
Carborundum (See Silicon Carbide)			
Caustic Potash (See Potassium Hydroxide)			
Soda (See Sodium Hydroxide)			
Ceric Nitrate	$Ce(NO_3)_4$	388.28	2.58915
Oxalate	$Ce(C_2O_4)_2$	316.25	2.50003
Oxide	CeO_2	172.25	2.23616
Cerous Nitrate, Anhydrous	$Ce(NO_3)_3$	326.27	2.51358
Nitrate, Crystalline	$Ce(NO_3)_3{\cdot}6H_2O$	434.37	2.63786
Oxide	Ce_2O_3	328.50	2.51654
Sulfate, Anhydrous	$Ce_2(SO_4)_3$	568.69	2.75487
Sulfate, Crystalline	$Ce_2(SO_4)_3{\cdot}8H_2O$	712.82	2.85298
Cesium Carbonate	Cs_2CO_3	325.62	2.51271
Chloride	$CsCl$	168.27	2.22601
Hydroxide	$CsOH$	149.82	2.17557
Nitrate	$CsNO_3$	194.82	2.28963
Sulfate	Cs_2SO_4	361.68	2.55833
(Chlorate Radical)	ClO_3	83.457	1.92146
Chloroform	$CHCl_3$	119.379	2.07693

TABLE AII—Molecular and Atomic-Group Weights—(*Continued*)

Name	Formula	Molecular Weight	Logarithm
(Chlorplatinate Radical)	$PtCl_6$	407.97	2.61063
(Chromate Radical)	CrO_4	116.01	2.06450
Chrome Alum (See Potassium Chrome Alum)			
Orange (See Lead Chromate, Basic)			
Yellow (See Lead Chromate)			
Chromic Chloride, Anhydrous	$CrCl_3$	158.38	2.19970
Chloride, Crystalline	$CrCl_3 \cdot 6H_2O$	266.48	2.42567
Hydroxide	$Cr(OH)_3$	103.03	2.01297
Nitrate, Anhydrous	$Cr(NO_3)_3$	238.03	2.37663
Nitrate, Crystalline	$Cr(NO_3)_3 \cdot 7\frac{1}{2}H_2O$	373.15	2.57189
Nitrate, Crystalline	$Cr(NO_3)_3 \cdot 9H_2O$	400.18	2.60226
Oxide	Cr_2O_3	152.02	2.18190
Sulfate, Anhydrous	$Cr_2(SO_4)_3$	392.21	2.59352
Sulfate, Crystalline	$Cr_2(SO_4)_3 \cdot 5H_2O$	482.29	2.68331
Chromium Trioxide	CrO_3	100.01	2.00004
Chromous Acetate, Anhydrous	$Cr(C_2H_3O_2)_2$	170.06	2.23060
Acetate, Crystalline	$Cr(C_2H_3O_2)_2 \cdot H_2O$	188.07	2.27432
Chloride	$CrCl_2$	122.92	2.08962
Oxide	CrO	68.01	1.83257
Sulfate, Anhydrous	$CrSO_4$	148.07	2.17047
Sulfate, Crystalline	$CrSO_4 \cdot 7H_2O$	274.19	2.43805
Citral	$C_9H_{15} \cdot CHO$	152.128	2.18221
Cobaltic Chloride	$CoCl_3$	165.31	2.21830
Hydroxide	$Co(OH)_3$	109.96	2.04123
Oxide	Co_2O_3	165.88	2.21980
Cobalto-cobaltic Oxide	Co_3O_4	240.82	2.38170
Cobaltous Chloride, Anhydrous	$CoCl_2$	129.85	2.11344
Chloride, Crystalline	$CoCl_2 \cdot 6H_2O$	237.95	2.37649
Nitrate, Anhydrous	$Co(NO_3)_2$	182.96	2.26235
Nitrate, Crystalline	$Co(NO_3)_2 \cdot 6H_2O$	291.05	2.46387
Oxide	CoO	74.94	1.87471
Sulfate, Anhydrous	$CoSO_4$	155.00	2.19033
Sulfate, Crystalline	$CoSO_4 \cdot 7H_2O$	281.12	2.44889
Copper (See also Cupric and Cuprous)			
Arsenate, Anhydrous	$Cu_3(AsO_4)_2$	468.63	2.67083
Arsenate, Crystalline	$Cu_3(AsO_4)_2 \cdot 4H_2O$	540.69	2.73295
Potassium Chloride (See Potassium Cupric Chloride)			
Potassium Sulfate (See Potassium Cupric Sulfate)			
Corrosive Sublimate (See Mercuric Chloride)			

TABLE AII—Molecular and Atomic-Group Weights—(*Continued*)

Name	Formula	Molecular Weight	Logarithm
Coumarin	$C_9H_6O_2$	146.048	2.16449
Cupric Aceto-arsenite	$Cu_3(AsO_3)_2 \cdot 2As_2O_3 \cdot Cu(C_2H_3O_2)_2$	1014.09	3.00608
Ammonium Chloride	$CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O$	277.51	2.44328
Arsenite	$CuHAsO_3$	187.54	2.27309
Carbonate	$CuCO_3$	123.57	2.09192
Carbonate, Basic	$CuCO_3 \cdot Cu(OH)_2$	221.16	2.34471
Carbonate, Basic	$2CuCO_3 \cdot Cu(OH)_2$	344.73	2.53748
Chloride, Anhydrous	$CuCl_2$	134.43	2.12866
Chloride, Crystalline	$CuCl_2 \cdot 2H_2O$	170.52	2.23177
Hydroxide	$Cu(OH)_2$	97.59	1.98941
Nitrate, Anhydrous	$Cu(NO_3)_2$	187.59	2.27321
Nitrate, Crystalline	$Cu(NO_3)_2 \cdot 3H_2O$	241.63	2.38315
Nitrate, Crystalline	$Cu(NO_3)_2 \cdot 6H_2O$	295.68	2.47082
Oxide	CuO	79.57	1.90075
Sulfate, Anhydrous	$CuSO_4$	159.63	2.20311
Sulfate, Crystalline	$CuSO_4 \cdot 5H_2O$	249.71	2.39744
Sulfide	CuS	95.63	1.98059
Cuprous Hydroxide	$CuOH$	80.58	1.90623
Oxide	Cu_2O	143.14	2.15576
Sulfide	Cu_2S	159.20	2.20194
Sulfocyanate	$CuCNS$	121.64	2.08507
(Cyanide Radical)	CN	26.008	1.41511
Cyanogen	C_2N_2	52.016	1.71614
Dextrose, Crystalline	$C_6H_{12}O_6 \cdot H_2O$	198.112	2.29691
Dimethylglyoxime	$(CH_3)_2C_2(NOH)_2$	116.080	2.06476
Erbium Oxide	Er_2O_3	383.4	2.58365
(Ethyl Radical)	C_2H_5	29.040	1.46300
Acetate	$C_2H_5C_2H_3O_2$	88.064	1.94480
Alcohol	C_2H_5OH	46.048	1.66321
Ferric (Ammonium) Alum	$Fe_2(NH_4)_2(SO_4)_4 \cdot 24H_2O$	964.40	2.98426
Chloride, Anhydrous	$FeCl_3$	162.21	2.21008
Chloride, Crystalline	$FeCl_3 \cdot 6H_2O$	270.31	2.43187
Ferrocyanide	$Fe_4[Fe(CN)_6]_3$	859.02	2.93400
Hydroxide	$Fe(OH)_3$	106.86	2.02882
Nitrate, Anhydrous	$Fe(NO_3)_3$	241.86	2.38357
Nitrate, Crystalline	$Fe(NO_3)_3 \cdot 9H_2O$	404.01	2.60639

TABLE AII—Molecular and Atomic-Group Weights—(*Continued*)

Name	Formula	Molecular Weight	Logarithm
Ferric Oxide	Fe_2O_3	159.68	2.20325
Oxide, Hydrated	$Fe_2O_3 \cdot H_2O$	177.70	2.24969
Phosphate, Anhydrous	$FePO_4$	150.87	2.17860
Potassium Alum (See Potassium Ferric Alum)			
Sulfate, Anhydrous	$Fe_2(SO_4)_3$	399.87	2.60192
Sulfate, Crystalline	$Fe_2(SO_4)_3 \cdot 9H_2O$	562.02	2.74975
Sulfide*	Fe_2S_3	207.87	2.31779
Ferroso-ferric Oxide	Fe_3O_4	231.52	2.36459
Sulfide	Fe_3S_4	295.78	2.47097
Ferrous Acetate, Anhydrous	$Fe(C_2H_3O_2)_2$	173.89	2.24028
Acetate, Crystalline	$Fe(C_2H_3O_2)_2 \cdot 4H_2O$	245.95	2.39085
Ammonium Sulfate	$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	392.14	2.59344
Carbonate	$FeCO_3$	115.84	2.06386
Chloride, Anhydrous	$FeCl_2$	126.75	2.10295
Chloride, Crystalline	$FeCl_2 \cdot 4H_2O$	198.82	2.29846
Ferricyanide	$Fe_3[Fe(CN)_6]_2$	591.30	2.77181
Hydroxide	$Fe(OH)_2$	89.86	1.95357
Oxide	FeO	71.84	1.85637
Sulfate, Anhydrous	$FeSO_4$	151.90	2.18156
Sulfate, Crystalline	$FeSO_4 \cdot 7H_2O$	278.02	2.44407
Sulfide	FeS	87.90	1.94399
(Fluosilicate Radical)	SiF_6	142.06	2.15247
Formaldehyde	HCHO	30.016	1.47735
Furfural	$C_4H_3O \cdot CHO$	96.032	1.98242
Fusel Oil (See Amyl Alcohol)			
Galactose	$C_6H_{12}O_6$	180.096	2.25550
Glauber Salts (See Sodium Sulfate, Crystalline)			
Glycerol	$C_3H_5(OH)_3$	92.064	1.96409
Glyceryl Trioleate	$C_3H_5(C_{18}H_{33}O_2)_3$	884.832	2.94686
Gold Chloride (See Auric Chloride)			
Gypsum (See Calcium Sulfate, Crystalline)			
Hydrogen Peroxide	H_2O_2	34.016	1.53168
Sulfide	H_2S	34.080	1.53250
(Hydroxyl Radical)	OH	17.008	1.23065
(Hypophosphate Radical)	PO_2	63.027	1.79953
(Iodate Radical)	IO_3	174.932	2.24287
Iodine Dioxide	IO_2	158.932	2.20121

* See also Iron Sulfide.

TABLE AII—Molecular and Atomic-Group Weights—(*Continued*)

Name	Formula	Molecular Weight	Logarithm
Iodine Monochloride	ICl	162.389	2.21056
Pentoxide	I_2O_5	333.864	2.52358
Trichloride	ICl_3	233.303	2.36792
Iron Alum (See Ferric Ammonium Alum)*			
Di-sulfide	FeS_2	119.97	2.07907
Oxide, Magnetic (See Ferroso-ferric Oxide)			
Sulfide	Fe_7S_8	647.39	2.81116
Lactose, Crystalline	$C_{12}H_{22}O_{11}\cdot H_2O$	360.192	2.55653
Lanthanum Oxide	La_2O_3	325.80	2.51295
Lead, Red	Pb_3O_4	685.60	2.83607
Lead, White (See Lead Carbonate, Hydrated)			
Lead Acetate, Anhydrous	$Pb(C_2H_3O_2)_2$	325.25	2.51222
Acetate, Basic	$Pb_2(C_2H_3O_2)_3\cdot OH$	608.48	2.78425
Acetate, Basic†	$3Pb(C_2H_3O_2)_2\cdot 2PbO$	1422.14	3.15294
Acetate, Crystalline	$Pb(C_2H_3O_2)_2\cdot 3H_2O$	379.30	2.57898
Acid Arsenate	$PbHAsO_4$	347.17	2.54054
Arsenate	$Pb_3(AsO_4)_2$	899.52	2.95401
Carbonate	$PbCO_3$	267.20	2.42684
Carbonate, Hydrated	$2PbCO_3\cdot Pb(OH)_2$	775.62	2.88965
Chloride	$PbCl_2$	278.11	2.44422
Chromate	$PbCrO_4$	323.21	2.50948
Chromate, Basic	$PbCrO_4\cdot PbO$	546.41	2.73752
Cyanide	$Pb(CN)_2$	259.22	2.41366
Hydroxide	$Pb(OH)_2$	241.22	2.38242
Iodide	PbI_2	461.06	2.66376
Molybdate	$PbMoO_4$	367.2	2.56490
Monoxide	PbO	223.20	2.34869
Nitrate	$Pb(NO_3)_2$	331.22	2.52012
Oleate	$Pb(C_{18}H_{33}O_2)_2$	769.73	2.88634
Peroxide	PbO_2	239.20	2.37876
Stearate	$Pb(C_{18}H_{35}O_2)_2$	773.76	2.88861
Sulfate	$PbSO_4$	303.26	2.48181
Sulfate, Basic	$PbSO_4\cdot PbO$	526.46	2.72137
Sulfide	PbS	239.26	2.37887
Tungstate	$PbWO_4$	455.2	2.65820
Levulose	$C_6H_{12}O_6$	180.096	2.25550

* For other compounds of iron, see under Ferric and Ferrous.

† Horne's reagent.

TABLE AII—Molecular and Atomic-Group Weights—(*Continued*)

Name	Formula	Molecular Weight	Logarithm
Lime (See Calcium Oxide)			
Litharge (See Lead Monoxide)			
Lithium Acetate, Anhydrous	$LiC_2H_3O_2$	65.964	1.81931
Acetate, Crystalline	$LiC_2H_3O_2 \cdot 2H_2O$	101.996	2.00858
Bromide	LiBr	86.856	1.93880
Carbonate	Li_2CO_3	73.880	1.86853
Chloride	LiCl	42.397	1.62734
Hydroxide	LiOH	23.948	1.37927
Nitrate, Anhydrous	$LiNO_3$	68.948	1.83852
Nitrate, Crystalline	$LiNO_3 \cdot 3H_2O$	122.996	2.08990
Oxide	Li_2O	29.880	1.46538
Phosphate, Anhydrous	Li_3PO_4	115.847	2.06388
Phosphate, Crystalline	$Li_3PO_4 \cdot H_2O$	133.863	2.12666
Sulfate, Anhydrous	Li_2SO_4	109.944	2.04117
Sulfate, Crystalline	$Li_2SO_4 \cdot H_2O$	127.960	2.10707
Magnesia (See Magnesium Oxide)			
Magnesium Acetate, Anhydrous	$Mg(C_2H_3O_2)_2$	142.37	2.15342
Acetate, Crystalline	$Mg(C_2H_3O_2)_2 \cdot 4H_2O$	214.43	2.33128
Acid Sulfite	$MgH_2(SO_3)_2$	186.46	2.26059
Ammonium Chloride	$MgCl_2 \cdot NH_4Cl \cdot 6H_2O$	256.83	2.40965
Ammonium Phosphate, Anhydrous	$MgNH_4PO_4$	137.39	2.13796
Ammonium Phosphate, Crystalline	$MgNH_4PO_4 \cdot 6H_2O$	245.48	2.39001
Ammonium Sulfate	$Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$	360.62	2.55705
Bicarbonate	$MgH_2(CO_3)_2$	146.34	2.16536
Bisulfite (Meta-)	MgS_2O_5	168.45	2.22647
Carbonate	$MgCO_3$	84.32	1.92593
Carbonate, Basic	$Mg(OH)_2 \cdot 4MgCO_3 \cdot 4H_2O$	467.68	2.66995
Chloride, Anhydrous	$MgCl_2$	95.23	1.97877
Chloride, Crystalline	$MgCl_2 \cdot 6H_2O$	203.33	2.30820
Hydroxide	$Mg(OH)_2$	58.34	1.76597
Nitrate, Anhydrous	$Mg(NO_3)_2$	148.34	2.17126
Nitrate, Crystalline	$Mg(NO_3)_2 \cdot 6H_2O$	256.43	2.40897
Oxide	MgO	40.32	1.60552
Phosphate, Anhydrous	$Mg_3(PO_4)_2$	263.01	2.41998

TABLE AII—Molecular and Atomic-Group Weights—(*Continued*)

Name	Formula	Molecular Weight	Logarithm
Magnesium Phosphate, Crystalline	$Mg_3(PO_4)_2 \cdot 4H_2O$	335.08	2.52514
Pyroarsenate	$Mg_2As_2O_7$	310.56	2.49214
Pyrophosphate	$Mg_2P_2O_7$	222.69	2.34770
Silicate (Meta-)	$MgSiO_3$	100.38	2.00164
Silicate (Ortho-)	$MgSiO_4$	116.38	2.06588
Sulfate, Anhydrous	$MgSO_4$	120.38	2.08056
Sulfate, Crystalline	$MgSO_4 \cdot 7H_2O$	246.50	2.39182
Sulfite, Anhydrous	$MgSO_3$	104.38	2.01862
Sulfite, Crystalline	$MgSO_3 \cdot 6H_2O$	212.48	2.32732
Maltose, Crystalline	$C_{12}H_{22}O_{11} \cdot H_2O$	360.192	2.55653
Manganese Carbonate	$MnCO_3$	114.93	2.06043
Chloride, Anhydrous	$MnCl_2$	125.84	2.09982
Chloride, Crystalline	$MnCl_2 \cdot 4H_2O$	197.91	2.29647
Dioxide	MnO_2	86.93	1.93917
Heptoxide	Mn_2O_7	221.86	2.34608
Hydroxide	$Mn(OH)_2$	88.95	1.94915
Nitrate, Anhydrous	$Mn(NO_3)_2$	178.95	2.25273
Nitrate, Crystalline	$Mn(NO_3)_2 \cdot 6H_2O$	287.04	2.45794
Pyrophosphate	$Mn_2P_2O_7$	283.91	2.45319
Silicate	$MnSiO_3$	130.99	2.11724
Sulfate, Anhydrous	$MnSO_4$	150.99	2.17895
Sulfate, Crystalline	$MnSO_4 \cdot 4H_2O$	223.06	2.34842
Sulfide	MnS	86.99	1.93947
Trioxide	MnO_3	102.93	2.01255
Manganic Oxide	Mn_2O_3	157.86	2.19827
Mangano-manganic Oxide	Mn_3O_4	228.79	2.35944
Manganous Oxide	MnO	70.93	1.85083
Menthol	$C_{10}H_{19}OH$	156.160	2.19357
Menthyl Acetate	$C_{10}H_{19}C_2H_3O_2$	198.176	2.29704
Mercuric Bromide	$HgBr_2$	360.44	2.55683
Chloride	$HgCl_2$	271.52	2.43380
Cyanide	$Hg(CN)_2$	252.63	2.40248
Hydroxide	$Hg(OH)_2$	234.63	2.37038
Iodide	HgI_2	454.47	2.65750
Nitrate, Anhydrous	$Hg(NO_3)_2$	324.63	2.51139
Nitrate, Crystalline	$Hg(NO_3)_2 \cdot H_2O$	342.64	2.53484
Oxide	HgO	216.61	2.33568
Sulfate	$HgSO_4$	296.67	2.47228
Sulfide	HgS	232.67	2.36674

TABLE AII—Molecular and Atomic-Group Weights—(*Continued*)

Name	Formula	Molecular Weight	Logarithm
Mercurous Chloride	Hg_2Cl_2	472.13	2.67406
Mercury Fulminate	$HgC_2N_2O_2$	284.63	2.45428
Methane	CH_4	16.032	1.20498
(Methyl Radical)	CH_3	15.024	1.17679
Acetate	$CH_3C_2H_3O_2$	74.048	1.86952
Alcohol	CH_3OH	32.032	1.50559
Salicylate	$CH_3C_7H_5O_3$	152.064	2.18202
Microcosmic Salt (See Ammonium Sodium Hydrogen Phosphate, Crystalline)			
Minium (See Lead, Red)			
(Molybdate Radical)	MoO_4	160.0	2.20412
Molybdic Dioxide	MoO_2	128.0	2.10721
Oxide	Mo_2O_3	240.0	2.38021
Sulfide	MoS_2	160.1	2.20439
Trioxide	MoO_3	144.0	2.15836
Neodymium Oxide	Nd_2O_3	336.54	2.52704
Nickel Ammonium Chloride	$NiCl_2 \cdot NH_4Cl \cdot 6H_2O$	291.20	2.46419
Carbonate	$NiCO_3$	118.69	2.07441
Chloride, Anhydrous	$NiCl_2$	129.60	2.11261
Chloride, Crystalline	$NiCl_2 \cdot 6H_2O$	237.70	2.37603
Cyanide, Anhydrous	$Ni(CN)_2$	110.71	2.04419
Cyanide, Crystalline	$Ni(CN)_2 \cdot 4H_2O$	182.77	2.26191
Glyoxime	$NiC_8H_{14}N_4O_4$	288.83	2.46065
Nitrate, Anhydrous	$Ni(NO_3)_2$	182.71	2.26176
Nitrate, Crystalline	$Ni(NO_3)_2 \cdot 6H_2O$	290.80	2.46359
Oxide	NiO	74.69	1.87326
Sulfate, Anhydrous	$NiSO_4$	154.75	2.18963
Sulfate, Crystalline	$NiSO_4 \cdot 7H_2O$	280.87	2.44851
Sulfide	NiS	90.75	1.95785
Nickelic Hydroxide	$Ni(OH)_3$	109.71	2.04025
Nickelo-nickelic Oxide	Ni_3O_4	240.07	2.38034
Nickelous Hydroxide	$Ni(OH)_2$	92.71	1.96713
Nicotine	$C_{10}H_{14}N_2$	162.128	2.20986
(Nitrate Radical)	NO_3	62.008	1.79245
Nitric Oxide	NO	30.008	1.47724
Nitrogen Pentoxide	N_2O_5	108.016	2.03348
Tetroxide	NO_2	46.008	1.66283
Trioxide	N_2O_3	76.016	1.88091
Nitrous Oxide	N_2O	44.016	1.64361

TABLE AII—Molecular and Atomic-Group Weights—(*Continued*)

Name	Formula	Molecular Weight	Logarithm
Orpiment (See Arsenous Sulfide)			
(Oxalate Radical)	C_2O_4	88.000	1.94448
Ozone	O_3	48.000	1.68124
Palladium Monoxide	PdO	122.7	2.08884
Paris Green (See Cupric Aceto-arsenite)			
(Perchlorate Radical)	ClO_4	99.457	1.99764
(Permanganate Radical)	MnO_4	118.93	2.07529
Phloroglucinol, Crystalline	$C_6H_3(OH)_3 \cdot 2H_2O$	162.080	2.20973
(Phosphate Radical)	PO_4	95.027	1.97786
(Phosphate Radical, Pyro-)	P_2O_7	174.054	2.24069
(Phosphite Radical)	PO_3	79.027	1.89778
Phosphoric Anhydride (See Phosphorus Pentoxide)			
Phosphorus Pentachloride	PCl_5	208.312	2.31872
Pentoxide	P_2O_5	142.054	2.15245
Trichloride	PCl_3	137.398	2.13798
Trioxide	P_2O_3	110.054	2.04161
Platinic Chloride, Anhydrous	$PtCl_4$	337.06	2.52771
Platinic Chloride, Crystalline	$PtCl_4 \cdot 5H_2O$	427.14	2.63057
Platinous Chloride	$PtCl_2$	266.14	2.42511
Potash (See Potassium Oxide)			
Alum (See Alum)			
Potassium Acetate	$KC_2H_3O_2$	98.120	1.99176
Acid Sulfate	$KHSO_4$	136.168	2.13408
Acid Sulfite	$KHSO_3$	120.168	2.07979
Aluminum Fluoride	K_3AlF_6	258.26	2.41206
Aluminum Silicate	$KAlSi_3O_8$	278.25	2.44444
Aluminum Sulfate (See Alum)			
Antimonyl Tartrate	$KSbOC_4H_4O_6 \cdot \frac{1}{2}H_2O$	333.91	2.52363
Bicarbonate	$KHCO_3$	100.104	2.00045
Bichromate	$K_2Cr_2O_7$	294.21	2.46866
Bifluoride	KHF_2	78.10	1.89265
Binoxolate	KHC_2O_4	128.104	2.10756
Bitartrate	$KHC_4H_4O_6$	188.136	2.27447
Bromide	KBr	119.012	2.07559
Carbonate	K_2CO_3	138.192	2.14048
Chlorate	$KClO_3$	122.553	2.08833
Chloride	KCl	74.553	1.87247
Chlorplatinate	K_2PtCl_6	486.16	2.68678
Chromate	K_2CrO_4	194.20	2.28825

TABLE AII—Molecular and Atomic-Group Weights—(*Continued*)

Name	Formula	Molecular Weight	Logarithm
Potassium Chrome Alum	$K_2Cr_2(SO_4)_4 \cdot 24H_2O$	998.85	2.99950
Cobaltinitrite, Anhydrous	$K_3Co(NO_2)_6$	452.28	2.65541
Cobaltinitrite, Crystalline	$K_3Co(NO_2)_6 \cdot 1\frac{1}{2}H_2O$	479.30	2.68061
Cupric Chloride	$K_2CuCl_4 \cdot 2H_2O$	319.62	2.50464
Cupric Sulfate	$K_2Cu(SO_4)_2 \cdot 6H_2O$	441.99	2.64541
Cyanide	KCN	65.104	1.81361
Ferric Alum	$K_2Fe_2(SO_4)_4 \cdot 24H_2O$	1006.51	3.00282
Ferricyanide	$K_3Fe(CN)_6$	329.18	2.51743
Ferrocyanide, Anhydrous	$K_4Fe(CN)_6$	368.27	2.56616
Ferrocyanide, Crystalline	$K_4Fe(CN)_6 \cdot 3H_2O$	422.32	2.62564
Fluoride	KF	58.10	1.76418
Fluosilicate	K_2SiF_6	220.25	2.34292
Hydrosulfide	KHS	72.168	1.85835
Hydroxide	KOH	56.104	1.74899
Iodate	KIO_3	214.028	2.33047
Iodide	KI	166.028	2.22018
Nitrate	KNO_3	101.104	2.00477
Nitrite	KNO_2	85.104	1.92995
Oleate	$KC_{18}H_{33}O_2$	320.360	2.50564
Oxalate, Anhydrous	$K_2C_2O_4$	166.192	2.22061
Oxalate, Crystalline	$K_2C_2O_4 \cdot H_2O$	184.208	2.26531
Oxide	K_2O	94.192	1.97401
Perchlorate	$KClO_4$	138.553	2.14162
Permanganate	$KMnO_4$	158.03	2.19874
Persulfate	$K_2S_2O_8$	270.320	2.43188
Phosphate, Di-	K_2HPO_4	174.227	2.24112
Phosphate, Mono-	KH_2PO_4	136.139	2.13398
Phosphate, (Ortho-)	K_3PO_4	212.315	2.32698
Silicate	K_2SiO_3	154.25	2.18823
Silver Cyanide (See Silver Potassium Cyanide)			
Sodium Carbonate, Anhydrous	$KNaCO_3$	122.093	2.08671
Sodium Carbonate, Crystalline	$KNaCO_3 \cdot 6H_2O$	230.189	2.36209
Sodium Tartrate	$KNaC_4H_4O_6 \cdot 4H_2O$	282.189	2.45054
Stearate	$KC_{18}H_{35}O_2$	322.376	2.50837
Sulfate	K_2SO_4	174.256	2.24119
Sulfide, Anhydrous	K_2S	110.256	2.04240
Sulfide, Crystalline	$K_2S \cdot 5H_2O$	200.336	2.30176
Sulfite, Anhydrous	K_2SO_3	158.256	2.19936
Sulfite, Crystalline	$K_2SO_3 \cdot 2H_2O$	194.288	2.28844

TABLE AII—Molecular and Atomic-Group Weights—(*Continued*)

Name	Formula	Molecular Weight	Logarithm
Potassium, Sulfocyanate	$KCNS$	97.168	1.98752
Tartrate, Anhydrous	$K_2C_4H_4O_6$	226.224	2.35453
Tartrate, Crystalline	$K_2C_4H_4O_6 \cdot \frac{1}{2}H_2O$	235.232	2.37150
Tetrasilicate	$K_2Si_4O_9$	334.43	2.52431
Xanthogenate	$KS_2COC_2H_5$	160.264	2.20483
Praseodymium Oxide	Pr_2O_3	329.84	2.51830
Prussian Blue (See Ferric Ferrocyanide)			
Prussic Acid (See Acid, Hydrocyanic)			
Pyrites (See Iron Disulfide)			
Pyrites, Magnetic (See Iron Sulfide)			
(Pyroarsenate Radical)	As_2O_7	261.92	2.41817
(Pyrophosphate Radical)	P_2O_7	174.054	2.24068
Radium Bromide	$RaBr_2$	385.78	2.58634
Chloride	$RaCl_2$	296.86	2.47255
Raffinose, Crystalline	$C_{18}H_{32}O_{16} \cdot 5H_2O$	594.336	2.77404
Realgar (See Arsenic Disulfide)			
Red Lead (See Lead, Red)			
Rhodium Chloride	$RhCl_3$	209.28	2.32073
Rochelle Salts (See Potassium Sodium Tartrate)			
Rubidium Oxide	Rb_2O	186.88	2.27156
Sulfate	Rb_2SO_4	266.94	2.42641
Ruthenium Oxide	Ru_2O_3	251.4	2.40037
Saccharin	$C_7H_5SO_3N$	183.112	2.26272
Sal Soda (See Sodium Carbonate, Decahydrate)			
Salt (See Sodium Chloride)			
Samarium Oxide	Sm_2O_3	348.86	2.54265
Scandium Oxide	Sc_2O_3	138.20	2.14051
Schlippe's Salt (See Sodium Thioantimonate)			
(Selenate Radical)	SeO_4	143.2	2.15594
(Selenite Radical)	SeO_3	127.2	2.10449
Selenium Dioxide	SeO_2	111.2	2.04610
Silica (See Silicon Dioxide)			
(Silicate Radical, Meta-)	SiO_3	76.06	1.88116
(Silicate Radical, Ortho-)	SiO_4	92.06	1.96407
(Silicate Radical, Tetra-)	Si_4O_9	256.24	2.40865
Silicon Carbide	SiC	40.06	1.60271
Dioxide	SiO_2	60.06	1.77859
Tetrafluoride	SiF_4	104.06	2.01728
Silver Bromide	$AgBr$	187.796	2.27368

TABLE AII—Molecular and Atomic-Group Weights—(*Continued*)

Name	Formula	Molecular Weight	Logarithm
Silver Carbonate	Ag_2CO_3	275.760	2.44053
Chloride	AgCl	143.337	2.15636
Chromate	Ag_2CrO_4	331.77	2.52084
Cyanide	AgCN	133.888	2.12674
Iodide	AgI	234.812	2.37072
Nitrate	$AgNO_3$	169.888	2.23016
Nitrite	$AgNO_2$	153.888	2.18721
Oxide	Ag_2O	231.760	2.36504
Potassium Cyanide	$AgK(CN)_2$	198.992	2.29883
Sodium Cyanide	$AgNa(CN)_2$	182.893	2.26219
Sulfate	Ag_2SO_4	311.824	2.49391
Sulfide	Ag_2S	247.824	2.39414
Sulfocyanate	AgSCN	165.952	2.21998
Thioantimonite	Ag_3SbS_3	541.60	2.73368
Thioarsenite	Ag_3AsS_3	494.79	2.69442
Soda (See Sodium Oxide)			
Alum (See Sodium Alum)			
Ash (See Sodium Carbonate, Anhydrous)			
Sodium Acetate, Anhydrous	$NaC_2H_3O_2$	82.021	1.91393
Acetate, Crystalline	$NaC_2H_3O_2 \cdot 3H_2O$	136.069	2.13376
Acid Hypophosphate, Anhydrous	$NaHPO_3$	103.032	2.01297
Acid Hypophosphate, Crystalline	$NaHPO_3 \cdot 3H_2O$	157.080	2.19612
Alum	$Na_2Al_2(SO_4)_4 \cdot 24H_2O$	916.57	2.96217
Aluminum Silicate	$NaAlSi_3O_8$	262.15	2.41855
Ammonium Hydrogen Phosphate (See Ammonium Sodium Hydrogen Phosphate)			
Arsenate, Di-, Anhydrous	Na_2HAsO_4	185.96	2.26942
Arsenate, Di-, Crystalline	$Na_2HAsO_4 \cdot 7H_2O$	312.07	2.49425
Arsenate, Tri-, Anhydrous	Na_3AsO_4	207.95	2.31796
Arsenate, Tri-, Crystalline	$Na_3AsO_4 \cdot 12H_2O$	424.14	2.62751
Arsenite, Di-	Na_2HAsO_3	169.96	2.23035
Arsenite, Tri-	Na_3AsO_3	191.95	2.28319
Benzoate	$NaC_7H_5O_2$	144.037	2.15847
Bicarbonate	$NaHCO_3$	84.005	1.92431
Bichromate, Anhydrous	$Na_2Cr_2O_7$	262.01	2.41832
Bichromate, Crystalline	$Na_2Cr_2O_7 \cdot 2H_2O$	298.05	2.47429

TABLE AII—Molecular and Atomic-Group Weights—(*Continued*)

Name	Formula	Molecular Weight	Logarithm
Sodium Binoxalate, Crystalline	$NaHC_2O_4 \cdot H_2O$	130.021	2.11401
Bisulfate	$NaHSO_4$	120.069	2.07943
Bisulfite	$NaHSO_3$	104.069	2.01732
Bisulfite (Meta-)	$Na_2S_2O_5$	190.122	2.27903
Bromate	$NaBrO_3$	150.913	2.17873
Bromide, Anhydrous	NaBr	102.913	2.01248
Bromide, Crystalline	$NaBr \cdot 2H_2O$	138.945	2.14284
Carbonate, Anhydrous	Na_2CO_3	105.994	2.02529
Carbonate, Decahydrate	$Na_2CO_3 \cdot 10H_2O$	286.154	2.45660
Carbonate, Monohydrate	$Na_2CO_3 \cdot H_2O$	124.010	2.09346
Chlorate	$NaClO_3$	106.454	2.02716
Chloride	NaCl	58.454	1.76681
Chromate, Anhydrous	Na_2CrO_4	162.00	2.20952
Chromate, Crystalline	$Na_2CrO_4 \cdot 10H_2O$	342.16	2.53423
Citrate, Anhydrous	$Na_3C_6H_5O_7$	258.031	2.41167
Citrate, Crystalline	$Na_3C_6H_5O_7 \cdot 5\frac{1}{2}H_2O$	356.119	2.55159
Cyanide	NaCN	49.005	1.69024
Fluoride	NaF	42.00	1.62325
Fluosilicate	Na_2SiF_6	188.05	2.27428
Hydrosulfide, Anhydrous	NaSH	56.069	1.74872
Hydrosulfide, Crystalline	$NaSH \cdot 2H_2O$	92.101	1.96427
Hydrosulfite	$Na_2S_2O_4$	174.122	2.24086
Hydroxide	NaOH	40.005	1.60212
Hypochlorite	NaOCl	74.454	1.87188
Hypophosphate, Anhydrous	Na_2PO_3	125.021	2.09698
Hypophosphate, Crystalline	$Na_2PO_3 \cdot 5H_2O$	215.101	2.33264
Hypophosphite, Anhydrous	NaH_2PO_2	88.040	1.94468
Hypophosphite, Crystalline	$NaH_2PO_2 \cdot H_2O$	106.056	2.02554
Hyposulfite	$NaHSO_2$	88.069	1.94483
Iodate	$NaIO_3$	197.929	2.29652
Iodide, Anhydrous	NaI	149.929	2.17589
Iodide, Crystalline	$NaI \cdot 2H_2O$	185.961	2.26942
Molybdate, Anhydrous	Na_2MoO_4	206.0	2.31387
Molybdate, Crystalline	$Na_2MoO_4 \cdot 2H_2O$	242.0	2.38382
Nitrate	$NaNO_3$	85.005	1.92945
Nitrite	$NaNO_2$	69.005	1.83888
Nitroprusside, Crystalline	$Na_2Fe(CN)_5NO \cdot 2H_2O$	297.91	2.47409
Oleate	$NaC_{18}H_{33}O_2$	304.261	2.48325

TABLE AII—Molecular and Atomic-Group Weights—(*Continued*)

Name	Formula	Molecular Weight	Logarithm
Sodium, Oxalate	$Na_2C_2O_4$	133.994	2.12708
Oxide	Na_2O	61.994	1.79235
Perchlorate	$NaClO_4$	122.454	2.08798
Peroxide	Na_2O_2	77.994	1.89206
Persulfate	$Na_2S_2O_8$	238.122	2.37680
Phosphate, Di-, Anhydrous	Na_2HPO_4	142.029	2.15238
Phosphate, Di-, Crystalline	$Na_2HPO_4 \cdot 12H_2O$	358.221	2.55416
Phosphate, Mono-, Anhydrous	NaH_2PO_4	120.040	2.07932
Phosphate, Mono-, Crystalline	$NaH_2PO_4 \cdot H_2O$	138.056	2.14005
Phosphate, Tri-, Anhydrous	Na_3PO_4	164.018	2.21489
Phosphate, Tri-, Crystalline	$Na_3PO_4 \cdot 12H_2O$	380.210	2.58002
Phosphite, Di-, Anhydrous	Na_2HPO_3	126.029	2.10046
Phosphite, Di-, Crystalline	$Na_2HPO_3 \cdot 5H_2O$	216.109	2.33467
Potassium Carbonate (See Potassium Sodium Carbonate)			
Potassium Tartrate (See Potassium Sodium Tartrate)			
Salicylate	$NaC_7H_5O_3$	160.037	2.20422
Silicate (Meta-)	Na_2SiO_3	122.05	2.08654
Silicate (Tetra-)	$Na_2Si_4O_9$	302.23	2.48034
Silver Cyanide (See Silver Sodium Cyanide)			
Stearate	$NaC_{18}H_{35}O_2$	306.277	2.48612
Sulfate, Anhydrous	Na_2SO_4	142.058	2.15246
Sulfate, Crystalline	$Na_2SO_4 \cdot 10H_2O$	322.218	2.50815
Sulfide, Anhydrous	Na_2S	78.058	1.89242
Sulfide, Crystalline	$Na_2S \cdot 9H_2O$	240.202	2.38057
Sulfite, Anhydrous	Na_2SO_3	126.058	2.10057
Sulfite, Crystalline	$Na_2SO_3 \cdot 7H_2O$	252.170	2.40170
Sulfocyanate	$NaCNS$	81.069	1.90886
Tartrate, Anhydrous	$Na_2C_4H_4O_6$	194.026	2.28786
Tartrate, Crystalline	$Na_2C_4H_4O_6 \cdot 2H_2O$	230.058	2.36184
Tetraborate, Anhydrous	$Na_2B_4O_7$	201.27	2.30378
Tetraborate, Crystalline	$Na_2B_4O_7 \cdot 10H_2O$	381.43	2.58141
Thioantimonate	$Na_3SbS_4 \cdot 9H_2O$	481.16	2.68229
Thiosulfate, Anhydrous	$Na_2S_2O_3$	158.122	2.19899
Thiosulfate, Crystalline	$Na_2S_2O_3 \cdot 5H_2O$	248.202	2.39480
Tungstate, Anhydrous	Na_2WO_4	294.0	2.46835
Tungstate, Crystalline	$Na_2WO_4 \cdot 2H_2O$	330.0	2.51851
Uranate	Na_2UO_4	348.16	2.54178
Vanadate, Anhydrous	Na_3VO_4	183.95	2.26470
Vanadate, Crystalline	$Na_3VO_4 \cdot 16H_2O$	472.21	2.67414

TABLE AII—Molecular and Atomic-Group Weights—(*Continued*)

Name	Formula	Molecular Weight	Logarithm
Stannic Chloride	$SnCl_4$	260.53	2.41586
Fluoride	SnF_4	194.70	2.28937
Oxide	SnO_2	150.70	2.17811
Phosphate, Anhydrous	$Sn_2P_2O_9$	443.45	2.64685
Phosphate, Crystalline	$Sn_2P_2O_9 \cdot 10H_2O$	623.61	2.79492
Sulfide	SnS_2	182.83	2.26205
Stannous Chloride, Anhydrous	$SnCl_2$	189.61	2.27786
Chloride, Crystalline	$SnCl_2 \cdot 2H_2O$	225.65	2.35344
Fluoride	SnF_2	156.70	2.19507
Hydroxide	$Sn(OH)_2$	152.72	2.18390
Oxide	SnO	134.70	2.12937
Sulfide	SnS	150.76	2.17828
Strontium Carbonate	$SrCO_3$	147.63	2.16918
Chloride, Anhydrous	$SrCl_2$	158.54	2.20014
Chloride, Crystalline	$SrCl_2 \cdot 6H_2O$	266.64	2.42592
Chromate	$SrCrO_4$	203.64	2.30886
Hydroxide, Anhydrous	$Sr(OH)_2$	121.65	2.08511
Hydroxide, Crystalline	$Sr(OH)_2 \cdot 8H_2O$	265.77	2.42450
Nitrate, Anhydrous	$Sr(NO_3)_2$	211.65	2.32562
Nitrate, Crystalline	$Sr(NO_3)_2 \cdot 4H_2O$	283.71	2.45288
Oxide	SrO	103.63	2.01549
Sulfate	$SrSO_4$	183.69	2.26409
Sulfide	SrS	119.69	2.07805
Sulfite	$SrSO_3$	167.69	2.22450
Thiosulfate	SrS_2O_3	199.76	2.30051
Sublimed Lead (See Lead Sulfate, Basic)			
Sucrose	$C_{12}H_{22}O_{11}$	342.176	2.53425
Sugar (See Sucrose)			
of Lead (See Lead Acetate, Crystalline)			
of Milk (See Lactose)			
(Sulfate Radical)	SO_4	96.064	1.98256
Sulfur Dioxide	SO_2	64.064	1.80661
Monochloride	S_2Cl_2	135.042	2.13047
Trioxide	SO_3	80.064	1.90344
Sulfuric Oxychloride	SO_2Cl_2	134.978	2.13026
Sulfurous Oxychloride	$SOCl_2$	118.978	2.07547
Tannin	$C_{14}H_{10}O_9$	322.080	2.50796
Tantalum Oxide	Ta_2O_5	443.0	2.64640
Tartar Emetic (See Potassium Antimonyl Tartrate)			

TABLE AII—Molecular and Atomic-Group Weights—(*Continued*)

Name	Formula	Molecular Weight	Logarithm
Tartaric Anhydride	$(C_4H_4O_4)_2O_2$	264.064	2.42171
Tellurium Dioxide	TeO_2	159.5	2.20276
Monoxide	TeO	143.5	2.15685
Trioxide	TeO_3	175.5	2.24428
Terbium Oxide	Tb_2O_3	366.4	2.56396
Thallic Oxide	Tl_2O_3	456.78	2.65971
Thallous Oxide	Tl_2O	424.78	2.62816
Theobromine	$C_7H_8N_4O_2$	180.096	2.25550
Thorium Nitrate, Anhydrous	$Th(NO_3)_4$	480.18	2.68140
Nitrate, Crystalline	$Th(NO_3)_4 \cdot 12H_2O$	696.37	2.84284
Oxide	ThO_2	264.15	2.42185
Tin Salt (See Stannous Chloride, Crystalline)*			
Titanium Dichloride	$TiCl_2$	119.0	2.07555
Dioxide	TiO_2	80.1	1.90363
Fluoride	TiF_4	124.1	2.09377
Peroxide	TiO_3	96.1	1.98272
Sulfate	$Ti_2(SO_4)_3$	384.4	2.58478
Tetrachloride	$TiCl_4$	189.9	2.27852
Toluene	$C_6H_5CH_3$	92.064	1.96409
Tungsten Dioxide	WO_2	216.0	2.33445
Disulfide	WS_2	248.1	2.39463
Trioxide	WO_3	232.0	2.36549
Trisulfide	WS_3	280.2	2.44747
Turnbull's Blue (See Ferrous Ferricyanide)			
Uranium Dioxide	UO_2	270.17	2.43164
Trioxide	UO_3	286.17	2.45663
(Urano-phosphate Radical)	$U_2P_2O_7$	650.39	2.81317
(Urano-phosphate Radical)	$U_2P_2O_{11}$	714.39	2.85393
Uranoso-uranic Oxide	U_3O_8	842.51	2.92558
Uranyl Acetate, Crystalline	$UO_2(C_2H_3O_2)_2 \cdot 2H_2O$	424.25	2.62762
Chloride	UO_2Cl_2	341.08	2.53285
Vanadium Dioxide	V_2O_2	133.92	2.12684
Oxysulfate	$V_2O_2(SO_4)_3$	422.11	2.62543
Pentoxide	V_2O_5	181.92	2.25988
Tetroxide	V_2O_4	165.92	2.21990
Trioxide	V_2O_3	149.92	2.17586
Vanadyl Chloride	$VOCl_2$	137.87	2.13947
Sulfate, Di-	$V_2O_2(SO_4)_2$	326.05	2.51329

* For other salts of Tin see under Stannic and Stannous.

TABLE AII—Molecular and Atomic-Group Weights—(*Concluded*)

Name	Formula	Molecular Weight	Logarithm
Vanillin	$C_8H_8O_3$	152.064	2.18203
Water	H_2O	18.016	1.25565
Glass (See Sodium Silicate, Tetra-)			
White Lead (See Lead Carbonate, Hydrated)			
Xylene	$C_6H_4(CH_3)_2$	106.080	2.02564
Xylose	$C_5H_{10}O_5$	150.080	2.17632
Ytterbium Oxide	Yb_2O_3	395.2	2.59682
Yttrium Oxide	Yt_2O_3	225.8	2.35372
Zinc Acetate, Anhydrous	$Zn(C_2H_3O_2)_2$	183.43	2.26347
Acetate, Crystalline	$Zn(C_2H_3O_2)_2{\cdot}2H_2O$	219.46	2.34135
Ammonium Phosphate	$ZnNH_4PO_4$	178.45	2.25152
Carbonate	$ZnCO_3$	125.38	2.09823
Chloride	$ZnCl_2$	136.29	2.13447
Ferrocyanide, Anhydrous	$Zn_2Fe(CN)_6$	342.65	2.53485
Ferrocyanide, Crystalline	$Zn_2Fe(CN)_6{\cdot}3H_2O$	396.70	2.59846
Hydroxide	$Zn(OH)_2$	99.40	1.99739
Mercury Sulfocyanate	$ZnHg(SCN)_4$	498.28	2.69747
Oxide	ZnO	81.38	1.91052
Pyrophosphate	$Zn_2P_2O_7$	304.81	2.48402
Sulfate, Anhydrous	$ZnSO_4$	161.44	2.20801
Sulfate, Crystalline	$ZnSO_4{\cdot}7H_2O$	287.56	2.45873
Sulfide	ZnS	97.44	1.98874
Zirconium Oxide	ZrO_2	123	2.08991
Pyrophosphate	ZrP_2O_7	265	2.42325

TABLE AIII

ANALYTICAL FACTORS

Wanted	Found	Factor	Logarithm
Ag	AgCl	0.7526	9.87656
AgCl	$BaCl_2$	1.3764	0.13874
	$CaCl_2$	2.5832	0.41215
	KCl	1.9226	0.28389
	$MgCl_2$	3.0104	0.47863
	NaCl	2.4522	0.38956
$AgNO_3$	Ag	1.5748	0.19722
	AgCl	1.1852	0.07379
Al	Al_2O_3	0.5291	9.72354
AlF_3	Al_2O_3	1.6474	0.21679
Al Oleate	Al_2O_3	17.08	1.23249
$Al(OH)_3$	Al_2O_3	1.5301	0.18472
Al_2O_3	$AlPO_4$	0.4177	9.62086
	$Al_2(SO_4)_3$	0.2980	9.47422
$Al_2(SO_4)_3$	Al_2O_3	3.3562	0.52585
	$BaSO_4$	0.4886	9.68895
	SO_3	1.4244	0.15363
$Al_2(SO_4)_3 \cdot 18H_2O$	Al_2O_3	6.5373	0.81540
	$BaSO_4$	0.9516	9.97845
	$CaCO_3$	2.2198	0.34631
	$MgCO_3$	2.6340	0.42062
	Na_2CO_3	2.0957	0.32133
As	As_2O_3	0.7575	9.87938
	As_2O_5	0.6520	9.81425
As_2O_3	As	1.3202	0.12063
	$Cu_3(AsO_3)_2.2As_2O_3 \cdot Cu(C_2H_3O_2)_2$	0.5855	9.76753
As_2O_5	As_2O_3	1.1617	0.06510
	$Pb_3(AsO_4)_2$	0.2556	9.40756
	$PbHAsO_4$	0.3311	9.51996
B	B_2O_3	0.3107	9.49240
$BaCO_3$	$BaSO_4$	0.8456	9.92716
$BaCl_2$	AgCl	0.7265	9.86124
	$BaSO_4$	0.8923	9.95051
BaO	$BaSO_4$	0.6570	9.81757
$Ba_3(PO_4)_2$	$BaSO_4$	0.8599	9.93445
	$Mg_2P_2O_7$	2.7040	0.43201
	P_2O_5	4.2390	0.62726
$BaSO_4$	$Ba_3(PO_4)_2$	1.1630	0.06558
Bi	BiOCl	0.8024	9.90439

TABLE AIII—Analytical Factors—(*Continued*)

Wanted	Found	Factor	Logarithm
C	CO_2	0.2727	9.43569
CO_2	$CaCO_3$	0.4397	9.64316
	CaO	0.7847	9.89470
	MgO	1.0913	0.03794
	Na_2CO_3	0.4151	9.61815
	$Pb(OH)_2{\cdot}2PbCO_3$	0.1135	9.05500
	SiO_2	0.7326	9.86487
Ca	$CaSO_4$	0.2943	9.46879
$Ca_3(AsO_4)_2$	As_2O_5	1.7316	0.23845
$CaCO_3$	Al_2O_3	2.9449	0.46908
	CO_2	2.2743	0.35685
	CaO	1.7847	0.25157
	$CaSO_4$	0.7351	9.86635
	Fe_2O_3	1.8800	0.27416
	$MgCO_3$	1.1868	0.07438
	MgO	2.4819	0.39478
$CaCl_2$	AgCl	0.3871	9.58782
	CaO	1.9793	0.29652
	Cl	1.5650	0.19451
$CaH_2(CO_3)_2$	$CaCO_3$	1.6197	0.20944
CaO	CO_2	1.2742	0.10524
	Ca	1.3993	0.14591
	$CaCO_3$	0.5603	9.74842
	$CaCl_2$	0.5052	9.70346
	$CaSO_4$	0.4119	9.61479
	$CaSO_4{\cdot}2H_2O$	0.3257	9.51282
$Ca(OH)_2$	CaO	1.3214	0.12103
	H_2O	4.1125	0.61411
Ca Oleate	CaO	10.750	1.03141
	Oleic Acid	1.0674	0.02832
$Ca_3(PO_4)_2$	$Mg_2P_2O_7$	1.3932	0.14401
	P_2O_5	2.1840	0.33925
$CaSO_4$	$BaSO_4$	0.5832	9.76582
	CaO	2.4279	0.38523
	SO_3	1.7004	0.23055
$CaSO_4{\cdot}2H_2O$	$BaSO_4$	0.7376	9.86782
	CaO	3.0706	0.48722
	$CaSO_4$	1.2647	0.10199
	SO_3	2.1504	0.33252

TABLE AIII—Analytical Factors—(*Continued*)

Wanted	Found	Factor	Logarithm
CaS_2O_5	CaO	3.2851	0.51655
	SO_2	1.4376	0.15764
$CaSiO_3$	CaO	2.0711	0.31620
	SiO_2	1.9335	0.28635
Casein	N	6.38	0.80482
Cd	$CdSO_4$	0.5392	9.73176
Ce	CeO_2	0.8142	9.91073
Cl	AgCl	0.2474	9.39334
	KCl	0.4756	9.67724
	NH_4Cl	0.6628	9.82138
	NaCl	0.6066	9.78290
	$NaClO_3$	0.3331	9.52257
	$ZnCl_2$	0.5203	9.71625
Cr_2O_3	$PbCrO_4$	0.2352	9.37144
Cu	CuO	0.7989	9.90249
CuO	Cu	1.2517	0.09750
	$Cu_3(AsO_3)_2 \cdot 2As_2O_3 \cdot Cu(C_2H_3O_2)_2$	0.3139	9.49679
$Cu(OH)_2$	CuO	1.2265	0.08867
F	CaF_2	0.4867	9.68726
Fat	Ca Soap	0.94	9.97313
	K Soap	0.88	9.94448
	Na Soap	0.93	9.96848
	Pb Soap	0.74	9.86923
Fatty Anhydride	Fatty Acid	0.9673	9.98556
Fe	$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	0.1424	9.15351
	Fe_2O_3	0.6994	9.84473
$FeCO_3$	Fe_2O_3	1.4509	0.16164
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	Fe_2O_3	4.9115	0.69122
Fe_2O_3	Fe	1.4298	0.15528
	$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	0.2036	9.30878
	$FePO_4$	0.5292	9.72362
	P_2O_5	1.1241	0.05081
$FeSO_4$	Fe_2O_3	1.9026	0.27935
$Fe_2(SO_4)_3$	Fe_2O_3	2.5042	0.39867
Glue	N	5.60	0.74819
Glycerol	$K_2Cr_2O_7$	0.1341	9.12743
Glyceryl Trioleate	Oleic Acid	1.0449	0.01908
H	H_2O	0.1119	9.04883

TABLE AIII—Analytical Factors—(*Continued*)

Wanted	Found	Factor	Logarithm
$HC_2H_3O_2$	$Cu_3(AsO_3)_2 \cdot 2As_2O_3 \cdot Cu(C_2H_3O_2)_2$	0.1184	9.07335
H_2CO_3	$KHCO_3$	0.3098	9.49108
	$NaHCO_3$	0.3691	9.56714
HCO_2H (Formic Acid)	Hg_2Cl_2	0.09747	8.98887
HCl	AgCl	0.2544	9.40552
HNO_3	N	4.4985	0.65307
	N_2O_3	1.6580	0.21958
$HNOSO_4$	N_2O_3	3.3435	0.52421
H_2O	$Al(OH)_3$	0.3465	9.53970
	$Ca(OH)_2$	0.2432	9.38596
	$CaSO_4$	0.2647	9.42275
	$CaSO_4 \cdot 2H_2O$	0.2093	9.32077
	$Mg(OH)_2$	0.3088	9.48968
H_2SO_4	$BaSO_4$	0.4202	9.62346
	$HNOSO_4$	0.7718	9.88750
	H_2O	5.4441	0.73593
	SO_3	1.2250	0.08814
$HgCl_2$	HgS	1.1670	0.06707
I	AgI	0.5406	9.73288
K	KCl	0.5244	9.71966
	$KClO_4$	0.2822	9.45056
	K_2O	0.8302	9.91918
	K_2PtCl_6	0.1608	9.20629
K_2CO_3	K_2O	1.4671	0.16646
KCl	AgCl	0.5201	9.71609
	Cl	2.1026	0.32276
	$KClO_4$	0.5381	9.73086
	K_2O	1.5830	0.19948
	K_2PtCl_6	0.3067	9.48671
$KHC_4H_4O_6$	K_2O	3.9948	0.60150
	$H_2C_4H_4O_6$	1.2538	0.09823
K_2O	K_2CO_3	0.6816	9.83353
	KCl	0.6317	9.80051
	$KClO_4$	0.3399	9.53135
	KOH	0.8394	9.92397
	K_2PtCl_6	0.1937	9.28713
	K_2SO_4	0.5405	9.73280
K_2SO_4	$BaSO_4$	0.7465	9.87303
	KCl	1.1686	0.06766

TABLE AIII—Analytical Factors—(*Continued*)

Wanted	Found	Factor	Logarithm
K_2SO_4	$KClO_4$	0.6288	9.79851
	K_2O	1.8500	0.26717
	K_2PtCl_6	0.3584	9.55437
	SO_3	2.1765	0.33776
Li	Li_2SO_4	0.1262	9.10106
Li_2O	Li_2SO_4	0.2656	9.42423
Menthol	Menthyl Acetate	0.7880	9.89653
Mg	$MgCO_3$	0.2884	9.46000
	$Mg_2P_2O_7$	0.2184	9.33925
$MgCO_3$	CO_2	1.9164	0.28249
	MgO	2.0915	0.32046
	$Mg_2P_2O_7$	0.7573	9.87927
$MgCl_2$	AgCl	0.3322	9.52140
	Cl	1.3429	0.12805
	MgO	2.3618	0.37324
$MgH_2(CO_3)_2$	$MgCO_3$	1.7355	0.23943
MgO	Mg	1.6579	0.21955
	$MgCl_2$	0.4234	9.62675
	$Mg_2P_2O_7$	0.3621	9.55883
	$MgSO_4$	0.3349	9.52492
$Mg(OH)_2$	MgO	1.4469	0.16044
$Mg(OH)_2{\cdot}4MgCO_3{\cdot}4H_2O$	$Mg_2P_2O_7$	0.8400*	9.92428
$Mg_3(PO_4)_2$	P_2O_5	1.8515	0.26753
$MgSO_4$	MgO	2.9857	0.47504
	$Mg_2P_2O_7$	1.0812	0.03391
	SO_3	1.5036	0.17713
MgS_2O_6	MgO	4.1778	0.62095
	SO_2	1.3147	0.11883
Mn	Fe	0.9837	9.99286
	Mn_3O_4	0.7203	9.85751
	$Mn_2P_2O_7$	0.3869	9.58760
$MnCO_3$	Mn_3O_4	1.5070	0.17811
$Mn_2P_2O_7$	MnO	2.0014	0.30133
Mo	$PbMoO_4$	0.2614	9.41731
N	$AgNO_2$	0.0910	8.95904
	$C_7H_8N_4O_2$ (theobromine)	0.3111	9.49290
	$C_8H_{10}N_4O_2$ (caffeine)	0.2887	9.46045

* The empirical factor 0.837 is used in the analysis of asbestos-magnesia insulating products (see p. 86).

TABLE AIII—Analytical Factors—(*Continued*)

Wanted	Found	Factor	Logarithm
NH_3	N	1.2159	0.08490
NH_4	N	1.2878	0.10985
NH_4Cl	AgCl	0.3732	9.57194
	N	3.8190	0.58195
$(NH_4)_2SO_4$	NH_3	3.8794	0.58876
	SO_3	1.6505	0.21761
Na	NaCl	0.3934	9.59483
	Na_2O	0.7419	9.87035
	Na_2SO_4	0.3238	9.51028
Na_2CO_3	$BaCO_3$	0.5370	9.72997
	CO_2	2.4090	0.38184
	Na	2.3046	0.36259
	$Na_2CO_3 \cdot H_2O$	0.8547	9.93181
	$NaHCO_3$	0.6309	9.79996
	Na_2O	1.7098	0.23295
	NaOH	1.3248	0.12215
	Na_2SO_4	0.7462	9.87286
NaCl	AgCl	0.4078	9.61045
	Cl	1.6486	0.21712
	Na	2.5417	0.40513
	Na_2O	1.8858	0.27549
$NaHCO_3$	CO_2	1.9092	0.28085
	Na_2CO_3	1.5851	0.20006
	Na_2O	2.7101	0.43299
Na_2HPO_4	P_2O_5	1.9997	0.30096
$NaNO_3$	N	6.0683	0.78307
	N_2O_5	1.5740	0.19700
Na_2O	$BaSO_4$	0.2656	9.42423
	Na	1.3479	0.12966
	Na_2CO_3	0.5849	9.76708
	NaCl	0.5303	9.72452
	$NaHCO_3$	0.3690	9.56703
	$NaNO_3$	0.3646	9.56182
	NaOH	0.7748	9.88919
	Na_2S	0.7942	9.89993
	Na_2SO_4	0.4364	9.63988
	Na_2SiO_3	0.5079	9.70578
	$Na_2Si_4O_9$	0.2051	9.31197
NaOCl	Cl*	1.0499	0.02115

* "Available" chlorine.

TABLE AIII—Analytical Factors—(*Continued*)

Wanted	Found	Factor	Logarithm
$NaOH$	Na_2CO_3	0.7548	9.87783
	Na_2O	1.2906	0.11079
Na_2S	$AgNO_3$	0.2297	9.36116
	Zn	1.1940	0.07700
Na_2SO_4	$BaSO_4$	0.6086	9.78433
	Na_2CO_3	1.3402	0.12717
	Na_2O	2.2914	0.36010
	SO_3	1.7743	0.24903
$Na_2SO_4 \cdot 10H_2O$	$BaSO_4$	1.3804	0.14000
	Na_2SO_4	2.2683	0.35570
Na_2SiO_3	Na_2O	1.9687	0.29418
	SiO_2	2.0321	0.30794
$Na_2Si_4O_9$	Na_2O	4.8752	0.68799
	SiO_2	1.2583	0.09979
Ni	Ni-glyoxime	0.2032	9.30792
	NiO	0.7858	9.89531
O	Cl	0.2256	9.35334
P	$(NH_4)_2HPO_4 \cdot 12MoO_3$	0.01668	8.22220
	$(NH_4)_3PO_4 \cdot 12MoO_3$	0.01653	8.21827
	P_2O_5	0.4368	9.64028
P_2O_5	$Mg_2P_2O_7$	0.6379	9.80475
	$(NH_4)_2HPO_4 \cdot 12MoO_3$	0.03818	8.58184
	$(NH_4)_3PO_4 \cdot 12MoO_3$	0.03784	8.57795
	P	2.2892	0.35969
Pb	$PbCrO_4$	0.6411	9.80693
	PbO_2	0.8662	9.93762
	PbO_2	0.8643*	9.93666
	$PbSO_4$	0.6833	9.83461
$PbCO_3$	CO_2	6.0729	0.78339
	$Pb(OH)_2 \cdot 2PbCO_3$	0.6890	9.83822
$PbCrO_4$	Cr_2O_3	4.2522	0.62861
	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$	0.8521	9.93049
	$PbCO_3$	1.2096	0.08265
PbO	$Pb_3(AsO_4)_2$	0.7444	9.87181
	$PbCrO_4$	0.6906	9.83923
	$PbHAsO_4$	0.6429	9.80814
	PbO_2	0.9331	9.96993
	Pb_3O_4	0.9767	9.98976
	$Pb(OH)_2 \cdot 2PbCO_3$	0.8633	9.93616
	$PbSO_4$	0.7360	9.86688

* Empirical factor when deposited on anode by electrolysis.

TABLE AIII—Analytical Factors—(*Continued*)

Wanted	Found	Factor	Logarithm
$Pb(OH)_2$	$PbCrO_4$	0.7464	9.87297
	$Pb(OH)_2 \cdot 2PbCO_3$	0.3110	9.49276
$Pb(OH)_2 \cdot 2PbCO_3$ (White Lead)	CO_2	8.8140	0.94517
	$PbCrO_4$	0.7999	9.90304
	$PbSO_4$	0.8526	9.93075
PbS	S	7.462	0.87286
$PbSO_4$	$BaSO_4$	1.2991	0.11364
	$PbCrO_4$	0.9383	9.97234
Pb Stearate	$PbSO_4$	2.5515	0.40680
Protein	N	6.25	0.79588
Protein (in wheat products)	N	5.70	0.75587
Pt	NaCl	1.6700	0.22272
$PtCl_4$	NaCl	2.8832	0.45987
	Pt	1.7265	0.23717
Rosin Anhydride	Rosin Acids	0.9732	9.98820
S	$BaSO_4$	0.1373	9.13767
	Na_2S	0.4108	9.61363
	$Na_2S \cdot 9H_2O$	0.1335	9.12548
	$Na_2S_2O_3$	0.4056	9.60810
Saccharin	$BaSO_4$	0.7844	9.89454
SO_2	$BaSO_4$	0.2744	9.43838
	CaS_2O_5	0.6956	9.84236
	MgS_2O_5	0.7606	9.88116
SO_3	$Al_2(SO_4)_3$	0.7020	9.84634
	$BaSO_4$	0.3430	9.53529
	Fe_2O_3 (from $FeSO_4$)	1.0028	0.00121
	$FeSO_4$	0.5271	9.72189
	$Fe_2(SO_4)_3$	0.6007	9.77866
	Na_2SO_4	0.5636	9.75097
SO_4	$BaSO_4$	0.4115	9.61437
	SO_3	1.1998	0.07911
Sb_2O_4	Sb	1.2628	0.10133
Si	SiO_2	0.4672	9.66950
SiO_2	$Na_2Si_4O_9$	0.7949	9.90031
Sn	SnO_2	0.7877	9.89636
SnO_2	Sn	1.2696	0.10366
Ti	TiO_2	0.6095	9.77851
V	Fe	0.9126	9.96028

TABLE AIII—Analytical Factors—(*Concluded*)

Wanted	Found	Factor	Logarithm
W	WO_3	0.7931	9.89933
Zn	$K_2Cr_2O_7$	0.6667	9.82393
	$ZnNH_4PO_4$	0.3664	9.56396
	ZnO	0.8034	9.90493
	$Zn_2P_2O_7$	0.4290	9.63246
$ZnCl_2$	$Zn_2P_2O_7$	0.8943	9.95148
ZnO	$ZnHg(SCN)_4$	0.1633	9.21299
	$Zn_2P_2O_7$	0.5340	9.72754
	ZnS	0.8352	9.92179
ZnS	ZnO	1.1974	0.07824
$ZnSO_4$	$BaSO_4$	0.6916	9.83985
	SO_3	2.0164	0.30458
	ZnO	1.9838	0.29750
	$Zn_2P_2O_7$	1.0593	0.02502
ZrO_2	ZrP_2O_7	0.4642	9.66671

TABLE AIV

VOLUMETRIC SOLUTIONS

1 cc. of 1.0 N HCl is equivalent to:

Substance	Gram	Logarithm
Amyl Acetate,* $C_5H_{11}C_2H_3O_2$	0.13011	9.11431–10
$BaCO_3$†	0.09869	8.99427
$Ba(OH)_2$	0.08570	8.93298
Bornyl Acetate,* $C_{10}H_{17}C_2H_3O_2$	0.19616	9.29261
$Ca(C_{18}H_{33}O_2)_2$	0.3013	9.47900
$Ca(C_{18}H_{35}O_2)_2$	0.3033	9.48187
$CaCO_3$†	0.05004	8.69932
CaO	0.02804	8.44778
$Ca(OH)_2$	0.03705	8.56879
Casein (N × 6.38)	0.08937	8.95119
Ethyl Acetate,* $C_2H_5C_2H_3O_2$	0.08806	8.94478
Glue (N × 5.60)	0.07844	8.89454
HCl	0.03647	8.56194
$KC_{18}H_{33}O_2$	0.3204	9.50569
$KC_{18}H_{35}O_2$	0.3224	9.50840
K_2CO_3†	0.06910	8.83948
$KHCO_3$†	0.10010	9.00043
KNO_3	0.10110	9.00475
K_2O	0.04710	8.67302
KOH	0.05610	8.74896
Menthyl Acetate,* $C_{10}H_{19}C_2H_3O_2$	0.19818	9.29706
Methyl Acetate,* $CH_3C_2H_3O_2$	0.07405	8.86953
$MgCO_3$†	0.04216	8.62490
MgO†	0.02016	8.30449

* By saponification with caustic solution.

† Methyl orange indicator.

TABLE AIV—Volumetric Solutions—(*1.0 N HCl—Continued*)

1 cc. of 1.0 N HCl is equivalent to:

Substance	Gram	Logarithm
$Na_2B_4O_7$†	0.10064	9.00277–10
$Na_2B_4O_7 \cdot 10H_2O$†	0.1907	9.28035
$NaC_2H_3O_2$	0.08202	8.91392
$NaC_2H_3O_2 \cdot 3H_2O$	0.13607	9.13376
$NaC_{18}H_{33}O_2$	0.3043	9.48330
$NaC_{18}H_{35}O_2$	0.3063	9.48615
Na_2CO_3†	0.05300	8.72428
$Na_2CO_3 \cdot H_2O$†	0.06201	8.79246
$Na_2CO_3 \cdot 10H_2O$†	0.14308	9.15558
$Na_2C_2O_4$	0.13399	9.12707
$NaHCO_3$†	0.08401	8.92433
Na_2HPO_4†	0.14203	9.15238
$Na_2HPO_4 \cdot 12H_2O$†	0.3582	9.55413
Na_2O	0.03100	8.49136
NaOH	0.04001	8.60217
Na_3PO_4‡	0.16402	9.21489
Na_3PO_4†	0.08201	8.91387
Na_2S‡	0.07806	8.89243
$Na_2Si_4O_9$	0.1511	9.17926
N	0.014008	8.14638
NH_3	0.01703	8.23121
NH_4	0.01804	8.25624
$NH_4C_{18}H_{33}O_2$	0.2993	9.47611
NH_4Cl	0.05350	8.72835
$(NH_4)_2O$	0.02604	8.41564

* By saponification with caustic solution.

† Methyl orange indicator.

‡ Phenolphthalein indicator.

TABLE AIV—VOLUMETRIC SOLUTIONS—(*1.0 N HCl—Continued*)

1 cc. of 1.0 N HCl is equivalent to:

Substance	Gram	Logarithm
NH_4OH	0.03505	8.54469–10
Nicotine, $C_{10}H_{14}N_2$	0.1621	9.20978
Protein (N × 6.25)	0.08755	8.94226
Protein (N × 5.70)	0.07985	8.90227
Prussian Blue, $Fe_4[Fe(CN)_6]_3$	0.04772	8.67870
Tallow Oil‡	0.2877	9.45894
Wool Grease§	0.5501	9.74044

1 cc. of 0.5 N HCl is equivalent to:

Amyl Acetate,* $C_5H_{11}C_2H_3O_2$	0.06506	8.81331–10
$BaCO_3$†	0.04934	8.69320
$Ba(OH)_2$	0.04285	8.63195
Bornyl Acetate,* $C_{10}H_{17}C_2H_3O_2$	0.09808	8.99158
$Ca(C_{18}H_{33}O_2)_2$	0.1506	9.17782
$Ca(C_{18}H_{35}O_2)_2$	0.1517	9.18099
$CaCO_3$†	0.02502	8.39829
CaO	0.01402	8.14675
$Ca(OH)_2$	0.01852	8.26764
Casein (N × 6.38)	0.04469	8.65021
Ethyl Acetate,* $C_2H_5C_2H_3O_2$	0.04403	8.64375
Glue (N × 5.60)	0.03922	8.59351
HCl	0.018233	8.26086
$KC_{18}H_{33}O_2$	0.1602	9.20466
$KC_{18}H_{35}O_2$	0.1612	9.20737
K_2CO_3†	0.03455	8.53845

* By saponification with caustic solution.
† Methyl orange indicator.
‡ Saponification value 195.
§ Saponification value 102.

TABLE AIV—VOLUMETRIC SOLUTIONS—(*0.5 N HCl—Continued*)

1 cc. of 0.5 N HCl is equivalent to:

Substance	Gram	Logarithm
$KHCO_3$†	0.05005	8.69940–10
KNO_3	0.05055	8.70372
K_2O	0.02355	8.37199
KOH	0.02805	8.44793
Menthyl Acetate,* $C_{10}H_{19}C_2H_3O_2$	0.09909	8.99603
Methyl Acetate,* $CH_3C_2H_3O_2$	0.03702	8.56844
$MgCO_3$†	0.02108	8.32387
MgO†	0.01008	8.00346
N	0.007004	7.84535
NH_3	0.008516	7.93024
NH_4	0.009020	7.95521
$NH_4C_{18}H_{33}O_2$	0.1497	9.17522
NH_4Cl	0.02675	8.42732
$(NH_4)_2O$	0.01302	8.11461
NH_4OH	0.017524	8.24363
$Na_2B_4O_7$†	0.05032	8.70174
$Na_2B_4O_7 \cdot 10H_2O$†	0.09536	8.97937
$NaC_2H_3O_2$	0.04101	8.61289
$NaC_2H_3O_2 \cdot 3H_2O$	0.06803	8.83270
$NaC_{18}H_{33}O_2$	0.1521	9.18213
$NaC_{18}H_{35}O_2$	0.1531	9.18498
Na_2CO_3†	0.02650	8.42325
$Na_2CO_3 \cdot H_2O$†	0.03100	8.49136
$Na_2CO_3 \cdot 10H_2O$†	0.07154	8.85455

* By saponification with caustic solution.

† Methyl orange indicator.

TABLE AIV—Volumetric Solutions—(*0.5 N HCl—Continued*)

1 cc. of 0.5 N HCl is equivalent to:

Substance	Gram	Logarithm
$Na_2C_2O_4$	0.06700	8.82607–10
$NaHCO_3$†	0.04200	8.62325
Na_2HPO_4†	0.07101	8.85132
$Na_2HPO_4 \cdot 12H_2O$†	0.1791	9.25310
Na_2O	0.01550	8.19033
NaOH	0.020003	8.30110
Na_3PO_4‡	0.08201	8.91387
Na_3PO_4†	0.04100	8.61278
Na_2S‡	0.03903	8.59140
$Na_2Si_4O_9$	0.07556	8.87829
Nicotine, $C_{10}H_{14}N_2$	0.08106	8.90881
Protein (N × 6.25)	0.04378	8.64128
Protein (N × 5.70)	0.03992	8.60119
Prussian Blue, $Fe_4[Fe(CN)_6]_3$	0.02386	8.37767
Tallow Oil§	0.1439	9.15806
Wool Grease‖	0.2750	9.43933

1 cc. of 1.0 N NaOH is equivalent to:

Abietic Acid,‡ $HC_{20}H_{29}O_2$	0.3022	9.48029–10
Acetic Anhydride,‡ $(CH_3CO)_2O$	0.05102	8.70774
$Al_2(SO_4)_3$	0.05702	8.75603
Amyl Acetate,* $C_3H_{11}C_2H_3O_2$	0.1301	9.11428

* By saponification.
† Methyl orange indicator.
‡ Phenolphthalein indicator.
§ Saponification value 195.
‖ Saponification value 102.

TABLE AIV—Volumetric Solutions—(*1.0 N NaOH—Continued*)

1 cc. of 1.0 N NaOH is equivalent to:

Substance	Gram	Logarithm
B_2O_3‡	0.03482	8.54183-10
B_4O_7‡	0.03882	8.58906
Benzoic Acid,‡ $HC_7H_5O_2$	0.12205	9.08654
Bornyl Acetate,* $C_{10}H_{17}C_2H_3O_2$	0.19616	9.29261
Butyric Acid,‡ $HC_4H_7O_2$	0.08806	8.94478
CO_2‡	0.04400	8.64345
$Ca(C_2H_3O_2)_2$	0.07906	8.89796
$Ca(C_{18}H_{33}O_2)_2$	0.3013	9.47900
$Ca(C_{18}H_{35}O_2)_2$	0.3033	9.48187
Citric Acid, Anhydrous, $H_3C_6H_5O_7$	0.06402	8.80632
Citric Acid, Crystalline, $H_3C_6H_5O_7 \cdot H_2O$	0.07003	8.84528
Cl	0.03546	8.54974
Ethyl Acetate,* $C_2H_5C_2H_3O_2$	0.08806	8.94478
Formaldehyde, HCOH	0.03002	8.47741
Formic Acid,‡ HCO_2H	0.04602	8.66295
Glycerol,§ $C_3H_5(OH)_3$	0.03069	8.48700
H_3BO_3‡	0.06184	8.79127
HBr	0.08092	8.90806
$HC_2H_3O_2$‡	0.06003	8.77837
$H_2C_2O_4$‡	0.04501	8.65331
$H_2C_2O_4 \cdot 2H_2O$‡	0.06302	8.79948
HCl	0.03647	8.56194
HI	0.12794	9.10701
HNO_3	0.06302	8.79948

* By saponification.
† Methyl orange indicator.
‡ Phenolphthalein indicator.
§ By saponification after acetylization.

TABLE AIV—Volumetric Solutions—(*1.0 N NaOH—Continued*)

1 cc. of 1.0 N NaOH is equivalent to:

Substance	Gram	Logarithm
H_3PO_4‡	0.04903	8.69046–10
H_3PO_4†	0.09805	8.99145
H_2SO_3‡	0.04104	8.61321
H_2SO_4	0.04904	8.69055
$KC_{18}H_{33}O_2$	0.3204	9.50569
$KC_{18}H_{35}O_2$	0.3224	9.50840
$KHCO_3$	0.10010	9.00043
KHC_2O_4‡	0.12810	9.10755
$KHC_4H_4O_6$‡	0.18814	9.27448
K_2O	0.04710	8.67302
Lactic Acid,‡ $HC_3H_5O_3$	0.09005	8.95448
Malic Acid,‡ $H_2C_4H_4O_5$	0.06702	8.82620
Menthol,§ $C_{10}H_{19}OH$	0.15616	9.19357
Menthyl Acetate,* $C_{10}H_{19}C_2H_3O_2$	0.19818	9.29706
Methyl Acetate,* $CH_3C_2H_3O_2$	0.07405	8.86953
N	0.014008	8.14638
NO_3	0.06201	8.79246
N_2O_5	0.05401	8.73247
$Na_2B_4O_7$‡	0.05032	8.70174
$Na_2B_4O_7 \cdot 10H_2O$‡	0.09536	8.97937
$NaC_7H_5O_2$	0.14404	9.15848
$NaC_7H_5O_3$	0.16004	9.20423
$NaC_{18}H_{33}O_2$	0.3043	9.48330
$NaC_{18}H_{35}O_2$	0.3063	9.48615

* By saponification.
† Methyl orange indicator.
‡ Phenolphthalein indicator.
§ By saponification after acetylization.

TABLE AIV—VOLUMETRIC SOLUTIONS—(*1.0 N NaOH—Continued*)

1 cc. of 1.0 N NaOH is equivalent to:

Substance	Gram	Logarithm
$NaHCO_3$	0.08401	8.92433–10
Na_2O	0.03100	8.49136
NaOH	0.04001	8.60217
Oleic Acid,† $HC_{18}H_{33}O_2$	0.2823	9.45071
$Pb(C_2H_3O_2)_2 \cdot 3H_2O$	0.18965	9.27796
Salicylic Acid,† $HC_7H_5O_3$	0.13805	9.14004
SO_2†	0.03203	8.50556
SO_3	0.04003	8.60239
SO_4	0.04803	8.68151
Stearic Acid,† $HC_{18}H_{35}O_2$	0.2843	9.45378
Tallow Oil‡	0.2877	9.45894
Tartaric Acid, Anhydrous,† $H_2C_4H_4O_6$	0.07502	8.87518
Tartaric Acid, Crystalline,† $H_2C_4H_4O_6 \cdot H_2O$	0.08403	8.92443
Wool Grease§	0.5501	9.74044
1 cc. of 0.5 N NaOH is equivalent to:		
Abietic Acid,† $HC_{20}H_{29}O_2$	0.1511	9.17926–10
Acetic Anhydride,† $(CH_3CO)_2O$	0.02551	8.40671
$Al_2(SO_4)_3$	0.02851	8.45500
Amyl Acetate,* $C_5H_{11}C_2H_3O_2$	0.06506	8.81331

* By saponification.

† Phenolphthalein indicator.

‡ Saponification value 195.

§ Saponification value 102.

TABLE AIV—Volumetric Solutions—(*0.5 N NaOH—Continued*)

1 cc. of 0.5 N NaOH is equivalent to:

Substance	Gram	Logarithm
Benzoic Acid,† $HC_7H_5O_2$	0.06102	8.78547–10
B_2O_3†	0.01741	8.24080
B_4O_7†	0.01941	8.28803
Bornyl Acetate,* $C_{10}H_{17}C_2H_3O_2$	0.09808	8.99158
Butyric Acid,† $HC_4H_7O_2$	0.04403	8.64375
CO_2†	0.02200	8.34242
$Ca(C_2H_3O_2)_2$	0.03953	8.59693
$Ca(C_{18}H_{33}O_2)_2$	0.1506	9.17782
$Ca(C_{18}H_{35}O_2)_2$	0.1517	9.18099
Citric Acid, Crystalline, $H_3C_6H_5O_7 \cdot H_2O$	0.03501	8.54419
Cl	0.01773	8.24871
Ethyl Acetate,* $C_2H_5C_2H_3O_2$	0.04403	8.64375
Formaldehyde, HCOH	0.01501	8.17638
Formic Acid,† HCO_2H	0.02301	8.36192
Glycerol,‡ $C_3H_5(OH)_3$	0.015344	8.18594
H_3BO_3†	0.03092	8.49024
HBr	0.04046	8.60703
$HC_2H_3O_2$†	0.03002	8.47741
$H_2C_2O_4$†	0.02250	8.35218
$H_2C_2O_4 \cdot 2H_2O$†	0.03151	8.49845

* By saponification.

† Phenolphthalein indicator.

‡ By saponification after acetylization.

TABLE AIV—VOLUMETRIC SOLUTIONS—(*0.5 N NaOH—Continued*)

1 cc. of 0.5 N NaOH is equivalent to:

Substance	Gram	Logarithm
HCl	0.018233	8.26086–10
HI	0.06397	8.80598
HNO_3	0.03151	8.49845
H_3PO_4 ‡	0.02451	8.38934
H_3PO_4†	0.04903	8.69046
H_2SO_3‡	0.02052	8.31218
H_2SO_4	0.02452	8.38952
$KC_{18}H_{33}O_2$	0.1602	9.20466
$KC_{18}H_{35}O_2$	0.1612	9.20737
$KHCO_3$	0.05005	8.69940
KHC_2O_4‡	0.06405	8.80652
K_2O	0.02355	8.37199
Lactic Acid,‡ $HC_3H_5O_3$	0.04502	8.65341
Malic Acid,‡ $H_2C_4H_4O_5$	0.03351	8.52517
Menthol,§ $C_{10}H_{19}OH$	0.07808	8.89254
Menthyl Acetate,* $C_{10}H_{19}C_2H_3O_2$	0.09909	8.99603
Methyl Acetate,* $CH_3C_2H_3O_2$	0.03702	8.56844
N	0.007004	7.84535
NO_3	0.03100	8.49136
N_2O_5	0.02700	8.43136
$Na_2B_4O_7$‡	0.02516	8.40071

* By saponification.

† Methyl orange indicator.

‡ Phenolphthalein indicator.

§ By saponification after acetylization.

TABLE AIV—VOLUMETRIC SOLUTIONS—(*0.5 N NaOH—Continued*)

1 cc. of 0.5 N NaOH is equivalent to:

Substance	Gram	Logarithm
$Na_2B_4O_7 \cdot 10H_2O$*	0.04768	8.67834–10
$NaC_7H_5O_2$	0.07202	8.85745
$NaC_7H_5O_3$	0.08002	8.90320
$NaC_{18}H_{33}O_2$	0.1521	9.18213
$NaC_{18}H_{35}O_2$	0.1531	9.18498
$NaHCO_3$	0.04200	8.62325
Na_2O	0.01550	8.19033
NaOH	0.020003	8.30110
Oleic Acid,* $HC_{18}H_{33}O_2$	0.1411	9.14953
$Pb(C_2H_3O_2)_2 \cdot 3H_2O$	0.09483	8.97695
Salicylic Acid,* $HC_7H_5O_3$	0.06902	8.83897
SO_2*	0.016016	8.20455
SO_3	0.020016	8.30138
SO_4	0.024016	8.38050
Stearic Acid,* $HC_{18}H_{35}O_2$	0.1421	9.15259
Tallow Oil†	0.1439	9.15806
Tartaric Acid, Anhydrous* $H_2C_4H_4O_6$	0.03751	8.57415
Tartaric Acid, Crystalline* $H_2C_4H_4O_6 \cdot H_2O$	0.04202	8.62346
Wool Grease‡	0.2750	9.43933

1 cc. of 0.1 N $AgNO_3$ is equivalent to:

Ag	0.010788	8.03294–10
$AgNO_3$	0.016989	8.23017
$BaCl_2$	0.010414	8.01762
$BaCl_2 \cdot 2H_2O$	0.012216	8.08693

* Phenolphthalein indicator.

† Saponification value 195.

‡ Saponification value 102.

TABLE AIV—VOLUMETRIC SOLUTIONS—(*0.1 N $AgNO_3$—Continued*)

1 cc. of 0.1 N $AgNO_3$ is equivalent to:

Substance	Gram	Logarithm
Br	0.007992	7.90266–10
$CaCl_2$	0.005549	7.74421
$CdCl_2$	0.009166	7.96218
CdI_2	0.01831	8.26269
Cl	0.003546	7.54974
CN*	0.005202	7.71617
$FeCl_2$	0.006338	7.80195
$FeCl_3$	0.005407	7.73296
HBr	0.008092	7.90806
HCl	0.003647	7.56194
HCN*	0.005403	7.73263
HI	0.012794	8.10701
I	0.012693	8.10356
KBr	0.011901	8.07559
KCl	0.007455	7.87245
KCN*	0.013021	8.11464
KI	0.016603	8.22019
K_2O	0.004710	7.67302
KSCN	0.009717	7.98753
LiCl	0.004240	7.62737
$MgCl_2$	0.004762	7.67779
$MgCl_2 \cdot 6H_2O$	0.010167	8.00719
NaBr	0.010291	8.01246
$NaBr \cdot 2H_2O$	0.013895	8.14286
NaCl	0.005845	7.76678
NaCN*	0.009801	7.99127

*Liebig Method (see p. 47).

TABLE AIV—VOLUMETRIC SOLUTIONS—*(0.1 N $AgNO_3$—Continued)*

1 cc. of 0.1 N $AgNO_3$ is equivalent to:

Substance	Gram	Logarithm
NaI	0.014993	8.17589–10
$NaI \cdot 2H_2O$	0.018596	8.26942
Na_2O	0.003100	7.49136
NH_4Br	0.009796	7.99105
NH_4Cl	0.005350	7.72835
NH_4I	0.014497	8.16128
NH_4SCN	0.007611	7.88144
$PbCl_2$	0.013906	8.14320
$SrCl_2$	0.007927	7.89911
$SrCl_2 \cdot 6H_2O$	0.013331	8.12486
Theobromine, $C_7H_8N_4O_2$	0.018010	8.25551
$ZnCl_2$	0.006815	7.83347

1 cc. of 0.1 N Iodine is equivalent to:

Acetone, $(CH_3)_2CO$	0.0009675	6.98565–10
As	0.003748	7.57380
AsO_3	0.006148	7.78873
As_2O_3	0.004948	7.69443
As_2O_5	0.005748	7.75952
Br	0.007992	7.90266
$CaOCl_2$ (Bleach)	0.006349	7.80271
Cl	0.003546	7.54974
CrO_3	0.003334	7.52297
Cr_2O_3	0.002534	7.40381
Cu	0.006357	7.80325
CuO	0.007957	7.90075
$CuSO_4$	0.015963	8.20311
$CuSO_4 \cdot 5H_2O$	0.024971	8.39744

TABLE AIV—VOLUMETRIC SOLUTIONS—(*0.1 N Iodine—Continued*)

1 cc. of 0.1 N Iodine is equivalent to:

Substance	Gram	Logarithm
Fe'''	0.005584	7.74695–10
Fe_2O_3	0.007984	7.90222
HNO_2	0.002351	7.37125
H_2S	0.001704	7.23147
H_2SO_3	0.004104	7.61321
Iodine	0.012693	8.10356
$KClO_3$	0.002043	7.31027
K_2CrO_4	0.006473	7.81111
$K_2Cr_2O_7$	0.004903	7.69046
$KMnO_4$	0.003161	7.49982
KNO_2	0.004252	7.62859
Na_2CrO_4	0.005400	7.73239
$Na_2Cr_2O_7$	0.004367	7.64018
$Na_2Cr_2O_7 \cdot 2H_2O$	0.004967	7.69609
$NaHSO_3$	0.005203	7.71625
$NaNO_2$	0.003450	7.53782
Na_2S	0.003903	7.59140
$Na_2S \cdot 9H_2O$	0.012010	8.07954
Na_2SO_3	0.006303	7.79955
$Na_2SO_3 \cdot 7H_2O$	0.012609	8.10069
$Na_2S_2O_3$	0.015812	8.19899
$Na_2S_2O_3 \cdot 5H_2O$	0.024820	8.39480
$Na_2S_2O_5$	0.004753	7.67697
$(NH_4)_2CrO_4$	0.005070	7.70501
Oxygen	0.0008000	6.90309
$PbCrO_4$	0.010774	8.03238

TABLE AIV—VOLUMETRIC SOLUTIONS—(*0.1 N Iodine—Continued*)

1 cc. of 0.1 N Iodine is equivalent to:

Substance	Gram	Logarithm
PbO_2	0.011960	8.07773–10
Pb_3O_4	0.034280	8.53504
S	0.001603	7.20493
SO_2	0.003203	7.50556
Sb	0.006089	7.78455
Sb_2O_3	0.007289	7.86267
Sn	0.005935	7.77342

1 cc. of 0.1 N $Na_2S_2O_3$ is equivalent to:

Acetone, $(CH_3)_2CO$	0.0009675	6.98565–10
Br	0.007992	7.90266
$CaOCl_2$ (Bleach)	0.006349	7.80271
Cl	0.003546	7.54974
CrO_3	0.003334	7.52297
Cr_2O_3	0.002534	7.40381
Cu	0.006357	7.80325
CuO	0.007957	7.90075
$CuSO_4$	0.015963	8.20311
$CuSO_4 \cdot 5H_2O$	0.024971	8.39744
HNO_2	0.002351	7.37125
Iodine	0.012693	8.10356
K_2CrO_4	0.006473	7.81111
$K_2Cr_2O_7$	0.004903	7.69046
Na_2CrO_4	0.005400	7.73239
$Na_2Cr_2O_7$	0.004367	7.64018
$Na_2Cr_2O_7 \cdot 2H_2O$	0.004967	7.69609
$NaNO_2$	0.003450	7.53782
NaOCl	0.003723	7.57089

TABLE AIV—VOLUMETRIC SOLUTIONS—(*0.1 N $Na_2S_2O_3$—Continued*)

1 cc. of 0.1 N $Na_2S_2O_3$ is equivalent to:

Substance	Gram	Logarithm
$Na_2S_2O_3$	0.015812	8.19899–10
$Na_2S_2O_3 \cdot 5H_2O$	0.024820	8.39480
$(NH_4)_2CrO_4$	0.005070	7.70501
$PbCrO_4$	0.010774	8.03238
PbO_2	0.011960	8.07773
Pb_3O_4	0.034280	8.53504
S	0.001603	7.20493
SO_2	0.003203	7.50556
Sb	0.006089	7.78455
Sb_2O_3	0.007289	7.86267
Sn	0.005935	7.77342

1 cc. of 0.1 N $KMnO_4$ is equivalent to:

BaO_2	0.008469	7.92783–10
$BaO_2 \cdot 8H_2O$	0.015675	8.19521
$CaCO_3$	0.005004	7.69932
CaO	0.0028035	7.44770
CaO_2	0.0036035	7.55672
$CaSO_4$	0.006807	7.83296
$CaSO_4 \cdot 2H_2O$	0.008609	7.93495
Fe	0.005584	7.74695
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	0.039214	8.59344
FeO	0.007184	7.85637
Fe_2O_3	0.007984	7.90222
Fe_3O_4	0.007717	7.88745
$FePO_4$	0.015087	8.17860
$FeSO_4$	0.015190	8.18156

TABLE AIV—VOLUMETRIC SOLUTIONS—(*0.1 N $KMnO_4$—Continued*)

1 cc. of 0.1 N $KMnO_4$ is equivalent to:

Substance	Gram	Logarithm
$FeSO_4 \cdot 7H_2O$	0.027802	8.44407–10
HCO_2H (Formic Acid)	0.002301	7.36192
$H_2C_2O_4$	0.004501	7.65331
$H_2C_2O_4 \cdot 2H_2O$	0.006302	7.79948
H_2O_2	0.003402	7.53173
Iodine	0.012693	8.10356
$KMnO_4$	0.003161	7.49982
KNO_2	0.004255	7.62890
$K_2Cr_2O_7$	0.004903	7.69046
$K_2S_2O_8$	0.013516	8.13085
Mn	0.0010986	7.04084
MnO	0.0014186	7.15186
MnO_2	0.004347	7.63819
MoO_3*	0.004800	7.68124
$Na_2C_2O_4$	0.006700	7.82607
$NaNO_2$	0.003450	7.53782
$Na_2S_2O_8$	0.011906	8.07577
$(NH_4)_2C_2O_4$	0.006204	7.79267
$(NH_4)_2C_2O_4 \cdot H_2O$	0.007105	7.85156
$(NH_4)_2S_2O_8$	0.011410	8.05729
N_2O_3	0.001900	7.27875
P*	0.000089	5.94939
P_2O_5*	0.000203	6.30750
Sb	0.006089	7.78455
Sn	0.005935	7.77342
Tannin, $C_{14}H_{10}O_9$	0.004157	7.61878

* From titration of yellow phosphomolybdate after reduction.

TABLE AIV—Volumetric Solutions—(*Concluded*)

1 cc. of 0.1 N $K_2Cr_2O_7$ is equivalent to:

Substance	Gram	Logarithm
CrO_3	0.003334	7.52297–10
Cr_2O_3	0.002534	7.40381
Fe''	0.005584	7.74695
FeO	0.007184	7.85637
Fe_3O_4	0.007717	7.88745
$FeSO_4$	0.015190	8.18156
$FeSO_4 \cdot 7H_2O$	0.027802	8.44407
Glycerol, $C_3H_5(OH)_3$	0.0006576	6.81796
$K_2Cr_2O_7$	0.004903	7.69046
$PbCrO_4$	0.010774	8.03238
Zn	0.003269	7.51441

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